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SUMMARIES OF ARTICLES PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 24, No. 2, February 1961

THE EFFECT OF VARIATIONS IN BAROMETRIC PRESSURE AND OTHER FACTORS ON THE EBULLIOSCOPIC DETERMINATION OF MOLECULAR WEIGHTS, WITH SPECIAL REFERENCE TO THE USE OF THE MENZIES DIFFERENTIAL THERMOMETER

A theoretical treatment of the effect of variations in barometric pressure and other factors on the ebullioscopic determination of molecular weights leads to general expressions relating the variations in barometric pressure with the ebullioscopic constant of the solvent and with the temperature sensitivity of the MENZIES differential thermometer. Since these variations can affect significantly the accuracy of ebullioscopic molecular weight determinations, a single comprehensive correction term is calculated for each of the usual combinations of ebullioscopic solvent and thermometer filling liquid; this term enables results obtained at different pressures to be corrected to standard atmospheric pressure, thus eliminating the pressure effect. Finally a statistical analysis of some experimental results illustrates the validity of the correction term for the combination of benzene as ebullioscopic solvent with benzene as thermometer filling liquid.

S. KAMINSKY, *Anal. Chim. Acta*, 24 (1961) 101-112

APPLICATION OF THE DOUBLE WITHDRAWAL COUNTERCURRENT EXTRACTION TECHNIQUE TO ANALYTICAL CHEMISTRY

Application of the double withdrawal countercurrent extraction technique to chemical analysis has been singularly neglected, probably because of the complexity and tediousness of the associated mathematics. Present day computer technology proved to be readily applicable to the problem and information is presented which indicates the possible importance of this separation method to chemical analysis.

J. O. HIBBITS, *Anal. Chim. Acta*, 24 (1961) 113-120

TITRIMETRIC METHODS FOR THE MICRODETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS BY THE RAPID COMBUSTION PROCEDURE

I. THE DETERMINATION OF INDIVIDUAL HALOGENS

A critical study has been carried out of titrimetric methods suitable for the microdetermination of each of the halogens, chlorine, bromine and iodine, in their possible organic combinations with the elements, oxygen, nitrogen and sulphur, following organic decomposition by the rapid empty tube combustion procedure.

J. E. FILDES AND A. M. G. MACDONALD, *Anal. Chim. Acta*, 24 (1961) 121-127

KINETICS OF DECOMPOSITION OF YTTRIUM, CEROUS AND ZIRCONYL OXALATES

The kinetics of the decomposition of yttrium, cerous and zirconyl oxalates have been studied thermogravimetrically and also by differential thermal analysis.

R. P. AGARWALA AND M. C. NAIK, *Anal. Chim. Acta*, 24 (1961) 128-133

ANION EXCHANGE STUDIES OF ZIRCONIUM(IV) IN CITRATE SOLUTION SEPARATION FROM MIXTURES

The anion exchange behaviour of zirconium(IV) in a citrate system is described. Nitric acid, hydrochloric acid, perchloric acid and ammonium chloride were tested as eluants on Dowex 21 K column. Zirconium is separated from fission product elements *e.g.*, barium, strontium, cadmium, caesium, molybdate and also from lead.

S. M. KHOPKAR AND A. K. DE, *Anal. Chim. Acta*, 24 (1961) 134-137

ION EXCHANGE RESINS IN STEEL ANALYSIS

The metals vanadium, chromium and molybdenum may be separated from the other constituents of steel by passing an acetate buffered solution of the steel through a strongly basic anion exchanger and selectively eluting the above metals from the resin column with aqueous solutions of 0.6 N sodium hydroxide, 8 N hydrochloric acid and 1 N hydrochloric acid, respectively.

F. M. HALL AND A. BRYSON, *Anal. Chim. Acta*, 24 (1961) 138-142

USE OF CARBOXYLIC ACID CATION EXCHANGE RESIN IN THE ANALYSIS OF COPPER IN CHROMATED WOOD PRESERVATIVE SOLUTIONS

An ion exchange separation, using carboxylic acid resin, combined with a thiosulphate titration is suggested as a rapid and accurate method for the determination of copper in chromated wood preservatives.

R. A. EDGE, *Anal. Chim. Acta*, 24 (1961) 143-145

THE APPLICATION OF CHELATE SYSTEMS TO PARTITION CHROMATOGRAPHY: PRELIMINARY PAPER

It has been found possible to retain solutions of chelating agents on a solid supporting medium, and in this paper preliminary investigations are reported which were carried out to determine the extraction behaviour of radioactive copper between an aqueous hydrochloric acid phase and a solution of dithizone in an organic solvent retained on silica gel. Chloroform was found to be a very satisfactory solvent and carbon tetrachloride was also used. For both of these solvents the extraction *vs.* acidity curves were found to be similar to the corresponding liquid-liquid extraction. The high values for the fraction extracted show that this method would provide a useful technique for the concentration of copper from aqueous solution, and the similarity between the liquid-liquid and liquid-solid extractions suggests that it may be possible to adapt conventional liquid-liquid extractions to work on the column principle.

T. B. PIERCE, *Anal. Chim. Acta*, 24 (1961) 146-152

COLORIMETRIC DETERMINATION OF URANIUM(VI)

new, very sensitive reagent is proposed for the colorimetric determination of uranium(VI), namely 1-phenyl-3-methyl-4-(3'-carboxy-4'-hydroxyphenyl-azo)-pyrazol-5-one.

Gh. BAIULESCU AND I. C. CIUREA, *Anal. Chim. Acta*, 24 (1961) 152-154

UTILISATION OF PHENYLARSONIC ACID IN TURBIDIMETRY

DETERMINATION OF TANTALUM

(in French)

turbidimetric method is described for the determination of tantalum with phenylarsonic acid. The method is fast and rarely requires preliminary separation. The only interfering elements are cerium and niobium when present in molar ratios greater than Nb : Ta = 1 and Zr : Ta = 5.

R. SAINT-JAMES ET T. LECOMTE, *Anal. Chim. Acta*, 24 (1961) 155-160

THE RAPID SPECTROPHOTOMETRIC DETERMINATION OF COPPER IN NON-FERROUS ALLOYS

A very simple method has been established for the rapid determination of copper, employing the formation of the chlorocupric anion by means of concentrated hydrochloric acid. The absorption of the chlorocupric anion is measured spectrophotometrically at a wavelength of 950 m μ . The method is applicable to a wide variety of samples, including many non-ferrous alloys.

G. LINDLEY, *Anal. Chim. Acta*, 24 (1961) 161-166

THE SPECTROPHOTOMETRIC DETERMINATION OF MICROGRAM AMOUNTS OF CERIUM

A spectrophotometric procedure, which has a coefficient of variation of ca. 2%, is described for the determination of up to 80 μ g of cerium. Ceric ion formed by oxidation with persulphate, in the presence of catalytic amounts of silver, is reduced to the cerous state by treatment with excess ferrous-phenanthroline reagent. The decrease in optical density of the ferrous-phenanthroline compared with the reagent blank is a measure of the amount of cerium present. The only common cations which cause serious interference are Mn⁺² and Cr⁺³.

F. CULKIN AND J. P. RILEY, *Anal. Chim. Acta*, 24 (1961) 167-170

DETERMINATION OF TARTARIC ACID WITH LEAD TETRAACETATE

(in French)

It was found, that in a medium of 80% acetic acid, in the presence of potassium acetate the oxidation of tartaric acid by lead(IV)-acetate takes place quantitatively. In the indirect determination of tartaric acid and tartrates, an excess of lead(IV)-acetate is used, allowing 30 min for the reaction to take place. The remaining reagent is then determined by potentiometric titration with a volumetric hydroquinone solution.

A. BERKA, *Anal. Chim. Acta*, 24 (1961) 171-174

METHOD FOR DETERMINATION OF THE EQUIVALENCE POINT IN POTENTIOMETRIC TITRATIONS

method is developed for calculating the end-point and the ionization constant in a potentiometric titration. The influence of dilution is studied. The method is compared with the procedure KOLTHOFF and that of HAHN.

J. M. H. FORTUIN, *Anal. Chim. Acta*, 24 (1961) 175-191

POLAROGRAPHIC ANALYSIS USING POTASSIUM IODIDE AS A SUPPORTING ELECTROLYTE

III. THE POLAROGRAPHIC BEHAVIOR OF TRIVALENT ARSENIC

polarography of arsenic(III) in 0.1 or 1.0 *M* potassium iodide solutions has been studied.

T. MATSUMAE AND R. NAKASHIMA, *Anal. Chim. Acta*, 24 (1961) 192-199

CONTRIBUTIONS TO THE COMPLEXOMETRIC DETERMINATION OF CATION MIXTURES

III. SIMULTANEOUS TITRATION OF IRON(III) AND ALUMINIUM IN THE PRESENCE OF AMMONIUM THIOCYANATE AS INDICATOR

thiocyanate as indicator iron(III) and aluminium(III) can be titrated simultaneously if $[Al^{+3}]/[Al^{+3}] \leq 1/4$; iron(III) is titrated directly with EDTA, and aluminium(III) is determined back-titration of the excess of EDTA with cobalt nitrate solution in an acetone-water medium.

C. LITEANU, I. LUKÁCS AND C. STRUSIEVICI, *Anal. Chim. Acta*, 24 (1961) 200-202

CONCENTRATING TRACES OF COPPER FROM 1 *M* AMMONIUM CHLORIDE

(*Short Communication*)

R. TURSE AND WM. RIEMAN III, *Anal. Chim. Acta*, 24 (1961) 202-203

A RAPID AND SENSITIVE SUB-MICRO PHOSPHORUS DETERMINATION

(*Short Communication*)

C. J. F. BÖTTCHER, C. M. VAN GENT AND C. PRIES, *Anal. Chim. Acta*, 24 (1961) 203-204

THE EFFECT OF VARIATIONS IN BAROMETRIC PRESSURE AND OTHER FACTORS ON THE EBULLIOSCOPIC DETERMINATION OF MOLECULAR WEIGHTS, WITH SPECIAL REFERENCE TO THE USE OF THE MENZIES DIFFERENTIAL THERMOMETER

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INTRODUCTION

The ebullioscopic determination of the molecular weight of a substance, *i.e.* that involving the measurement of the elevation of the boiling point of a solvent by the substance, is a well established classical procedure; however, when results correct to $\pm 1-2\%$ or better are required, several effects which are usually ignored may become significant, especially when the boiling point elevation is measured with a MENZIES differential thermometer¹. Four such effects are considered below, *viz.*

- (1) the effect of reading only the level in the capillary limb of the MENZIES differential thermometer,
- (2) the effect of the ebullioscopic elevation on the sensitivity of the MENZIES differential thermometer,
- (3) the effect of variations in barometric pressure on the ebullioscopic constant of the solvent, and
- (4) the effect of variations in barometric pressure on the sensitivity of the MENZIES differential thermometer.

These effects are considered with special reference to the semi-micro and micro ebullioscopic methods of COLSON², since these possess several advantages (notably in the amount of sample required) over earlier methods; moreover, the semi-micro method has been extended in scope to cover a wider range of solvents and to include the use of a differential thermometer filled with benzene (instead of water) to obtain greater sensitivity when using low boiling solvents³. It is shown that while effects (1) and (2) are not significant in COLSON's methods, effects (3) and (4) are, *i.e.* although the small variations in barometric pressure normally encountered *during a single ebullioscopic experiment* using a MENZIES differential thermometer have no significant effect, the larger variations in barometric pressure *between different experiments* may be significant. Expressions are therefore developed to account for the effect of variations in barometric pressure, and correction terms allowing for this are calculated for use with some common solvent-thermometer combinations³.

THE MENZIES DIFFERENTIAL THERMOMETER

Since three of the four effects considered [(1), (2) and (4)] apply only when the MEN-

MENZIES differential thermometer is used, the main features of this thermometer are summarised.

The MENZIES differential thermometer in its usual form¹⁻⁵ is a U-tube manometer in which one limb is simply a bulb (the lower bulb); this connects by capillary tube (the capillary limb) to another bulb (the upper bulb). The thermometer is approximately half-filled with a liquid (usually water) and is sealed after evacuation so as to exclude air; it therefore contains only the filling liquid and its vapour. Differences in temperature between the lower and upper bulbs cause differences in vapour pressure in the bulbs, which in turn lead to differences in level between the liquid in the lower bulb and that in the capillary limb. In ebullioscopy the thermometer is positioned in the ebulliometer so that the lower bulb is subjected to the efflux of boiling solution from the Cottrell pump whereas the upper bulb is surrounded by solvent vapour. Initially, with a pure solvent boiling without super-heating, both bulbs are ideally at the same temperature and the difference in level between the liquid in the lower bulb and that in the capillary limb is simply the capillary rise due to surface tension; in practice the difference is usually increased slightly by unavoidable super-heating of the solvent and by the elevation of boiling point due to any residual impurities. On the addition of non-volatile solute the resulting elevation of boiling point causes the lower bulb to increase in temperature, whereas the upper bulb remains at the same temperature, *i.e.* at the boiling point of the solvent; this results in a rise of the liquid level in the capillary limb and a corresponding fall in the level in the lower bulb; the difference in height between the two levels can be measured if the thermometer has a scale engraved on it or if the levels are observed through a cathetometer. An important feature is that, unlike those ebulliometers where the elevation of boiling point is read on a single Beckmann thermometer surrounded by boiling solution, the small barometric fluctuations normally encountered *during the experiment* do not cause significant error, since both bulbs are affected equally. Moreover, at the temperatures encountered in ebullioscopy, the differential thermometer is more sensitive than the ordinary type of Beckmann thermometer, *e.g.* a 1-mm rise on a Beckmann thermometer represents a rise of approximately 0.01° but on a water-filled differential thermometer it represents about 0.005° at 80° and 0.002° at 110°. The other advantages of the differential thermometer over the Beckmann type are enumerated by MENZIES¹.

As shown by the preceding figures, the sensitivity of the differential thermometer, unlike the conventional mercury thermometer, increases markedly with temperature. It depends on the density-temperature and the vapour pressure-temperature relationships of the filling liquid; this is usually water, in which case temperature differences can be converted from mm head of water to ° by multiplying by the factor given by MENZIES in his conversion table¹ for temperatures up to 102°, and interpolating from the values calculated by KITSON AND MITCHELL⁵ for temperatures above 102°.

In certain instances it may be desirable to employ a filling liquid other than water in order to obtain greater sensitivity when using a low boiling solvent (*e.g.* benzene-filled thermometer with acetone as solvent^{3,5}). Although conversion tables for non-aqueous filling liquids do not appear in the literature, they may be constructed if the density-temperature and the vapour pressure-temperature relationships of the filling liquid are known⁵ (but see the footnote to equation 4.5 below).

PRELIMINARY CONSIDERATION OF THE MAGNITUDE OF THE EFFECTS

a) Effect of reading only the level in the capillary limb of the Menzies differential thermometer

The table of factors given by MENZIES¹ converts to °C the head of water measured in mm, *i.e.* the difference in levels between the menisci in the lower bulb and in the capillary limb. It is general practice, however, to observe only the level in the capillary limb; it is obvious that if this level rises the level in the lower bulb must fall by an amount depending on the ratio of the cross-sectional areas of the lower bulb and the capillary limb (the thermal expansion of the filling liquid can be ignored for the small temperature differences encountered). For example, the thermometer used in COLSON's semi-micro method² has a lower bulb approx. 7 mm in diameter and a 1-mm capillary, giving a cross-sectional ratio of approx. 50 : 1. A rise in the level of 1 mm in the capillary limb is therefore accompanied by a fall of approx. 0.02 mm in the level in the lower bulb and thus represents a total change of level of 1.02 mm. Although those operators who convert from mm head of water to °C usually observe only the level in the capillary limb, they obtain the total change of level by referring to a previously constructed graph relating the two values^{4,6}; this is considered to be both more convenient and more reliable than reading both levels. An alternative procedure for those thermometers which carry etched scales would be (by analogy with the Kew pattern barometer) to contract the scale on the capillary limb by an appropriate factor depending on the ratio of the cross-sectional areas of the lower bulb and capillary limb, *e.g.* by 0.98 in the above numerical example; the reading on the capillary limb would then represent directly the total change in level. However, this does not seem to have been attempted in the literature.

For COLSON's semi-micro method² and its extended modification³, in which a compound of known molecular weight is used as a standard and in which it is therefore unnecessary to convert the differential thermometer reading to °C, it seems preferable to adhere to his practice of observing only the rise in level in the capillary limb and recording this as the temperature elevation in mm. (Although COLSON converts the rise in level in the capillary limb directly to °C in his micro method², the constant error introduced cancels out when the molecular weight of the sample is compared with that of the standard compound). The practice of recording the temperature elevation in mm is in any case obligatory when using a thermometer filled with a non-aqueous liquid since there are then no published conversion tables.

The above arguments have a bearing on thermometer design and filling, in that it seems advisable not to make the lower bulb too narrow in diameter, so as to minimise the effect of any slight inconsistencies in bore, and neither to overfill nor underfill, so that the liquid meniscus never traverses the two ends of the bulb where the diameter necessarily becomes narrower.

b) The effect of the ebullioscopic elevation on the sensitivity of the Menzies differential thermometer

One effect arising from the temperature dependence of the sensitivity of the MENZIES differential thermometer is due to the fact that as the temperature of the lower bulb (in contact with the boiling solution) necessarily increases during the course of an ebullioscopic molecular weight determination, the sensitivity of the thermometer

correspondingly increases. Whether the increase is significant depends upon the magnitude of the temperature elevations encountered, which in turn depends upon the solute concentrations employed. When, as is generally the case in the literature, solute concentrations of 0.1 molal and over are used, corresponding to temperature elevations of 0.1–0.5° and over (depending upon the solvent employed), then the effect may become significant, *e.g.* taking benzene as ebullioscopic solvent with a water-filled thermometer, and assuming an elevation of 0.5°, then the temperature of the lower bulb is initially say 80.1° and finally 80.6°; the corresponding sensitivities are 4.952 and 4.910 · 10⁻³ °C/mm (the latter being the factor for the mean temperature of the upper and lower bulbs, *viz.* 80.35°) differ by 0.9%. The methods by which the effect is allowed for vary: thus MENZIES AND WRIGHT⁶ convert each reading of the differential thermometer from mm to °C by applying the appropriate factor corresponding to the mean temperature of the lower and upper bulbs, this temperature being higher than the initial boiling temperature (determined with an ordinary mercury thermometer) by half the observed temperature elevation. On the other hand BARR AND ANHORN⁴ calculate factors which allow simultaneously for both this effect and that described below (d) due to variations in barometric pressure on the sensitivity of the differential thermometer; however, their calculations (for which no details are given) refer only to the use of benzene as solvent with a water-filled differential thermometer in a limited pressure range (720–750 mm), and, moreover, they overcorrect for the effect of the ebullioscopic elevation by applying the MENZIES factor corresponding to the temperature of the lower bulb instead of the mean temperature of the upper and lower bulbs; they also ignore the effect described below (c) due to variations in barometric pressure on the ebullioscopic constant.

In COLSON's methods² the solute concentrations used are much lower than those described above (rarely exceeding 0.02 molal) and the total elevation rarely exceeds 0.1°. The difference in the factors in the example given above, *viz.* benzene as ebullioscopic solvent with water-filled thermometer, correspondingly rarely exceeds 0.2% and can therefore be neglected, as indeed it can in all the combinations of ebullioscopic solvent and thermometer filling liquid employed in the extended modification of the semi-micro method³.

(c) *The effect of variations in barometric pressure on the ebullioscopic constant*

Since an increase in barometric pressure increases the boiling point T of a solvent or solution, with a consequent decrease in the latent heat of vaporisation c_v , there will be an increase in the ebullioscopic constant K , from the fundamental relationship

$$K = RT^2/1000 c_v \quad (3)$$

where R is the gas constant; if R is in cal · mole⁻¹ · deg.⁻¹, T in °K and c_v in cal · g⁻¹ then K will be in deg. · mole⁻¹ · kg, *i.e.* deg. per mole of solute for 1000 g solvent. Similarly a decrease in barometric pressure will cause a decrease in the ebullioscopic constant. This increase (or decrease) can be calculated approximately in the following manner: Let the barometric pressure P increase by 10 mm from 760 to 770 mm Hg. Then the increase in boiling point ΔT will be, from Craft's rule⁷,

$$\Delta T = CT \cdot 10 \quad (3)$$

where T is the boiling point in $^{\circ}\text{K}$, and C is 0.00012 for most solvents and 0.00010 for water and alcohols. If now c_v is assumed to be independent of T , (3.1) transforms to

$$K\alpha T^2 \quad (3.3)$$

and the ratio of the ebullioscopic constants at 770 and 760 mm Hg will be given by

$$K_{770 \text{ mm}}/K_{760 \text{ mm}} = [(T + \Delta T)/T]^2, \quad (3.4)$$

$$\approx 1 + 2 \Delta T/T, \text{ as } \Delta T \text{ is small compared with } T \quad (3.4a)$$

$$\approx 1 + 20C$$

$$\approx 1.0024 \text{ for most solvents and } 1.0020 \text{ for water and alcohols.}$$

Hence K will increase by approximately 0.20–0.24% per 10 mm increase in pressure. Since c_v , which has been assumed independent of T , actually decreases with increase in T , the above estimate will be slightly low. The value generally quoted in the literature is approximately 0.3% per 10 mm⁶, and the more rigorous treatment given below yields values ranging from 0.21% (for ethanol) to 0.29% (for benzene) for eight solvents (Table I).

This effect is generally ignored in the literature, usually justifiably, since it is in general insignificant compared with the other deviations encountered in ebullioscopy, or it is sometimes inadvertently allowed for to some extent by determining the ebullioscopic constant (or a related apparatus constant) using a standard substance of known molecular weight under barometric conditions not differing markedly from those prevailing when the actual molecular weights of samples are being determined.

d) The effect of variations in barometric pressure on the sensitivity of the Menzies differential thermometer

The effect of variations in barometric pressure on the ebullioscopic constant treated in (c) is perfectly general and independent of the temperature-measuring device employed. However, when using a MENZIES differential thermometer there is a further effect, *viz.* that the variations in barometric pressure, in affecting the boiling point of the solvent or solution, affect the sensitivity of the thermometer. The magnitude of this effect will depend both on the temperature at which the differential thermometer is used and on the liquid with which it is filled; the appropriate expressions are derived below. However, it is instructive to ascertain the magnitude of the effect by calculating it for a typical set of circumstances, *e.g.* using benzene as ebullioscopic solvent with a water-filled thermometer. If, as before, it is assumed that the barometric pressure increases from 760 to 770 mm, then the boiling point of the benzene will increase by approximately 0.43° from 80.10 to 80.53° (*cf.* the value of dt/dp given in Table II below). The table of factors for the water-filled thermometer calculated by MENZIES¹ gives values of 4.952 and $4.879 \cdot 10^{-3} \text{ }^{\circ}\text{C}/\text{mm}$ respectively at these two temperatures. Denoting the ebullioscopic constant, expressed in the units mm rise on the water-filled thermometer per mole of solute for 1000 g solvent, as K' ,

$$K' \text{ (in mm/mole for 1000 g)} = K \text{ (in } ^{\circ}\text{C/mole for 1000 g)} / f \text{ (in } ^{\circ}\text{C/mm)} \quad (3.5)$$

Hence

$$K'_{770 \text{ mm}}/K'_{760 \text{ mm}} = f_{760 \text{ mm}}/f_{770 \text{ mm}} = 4.952/4.879 = 1.015$$

The above treatment ignores the effect of the increase in barometric pressure on K itself: however, this has been previously shown to be approx. 0.3% per 10 mm increase in pressure, so that the total effect of the 10 mm increase in pressure causes an increase of 1.8% in the ebullioscopic constant K' measured in mm/mole for 1000 g, the major part of the increase (1.5%) being due to the effect of the barometric pressure on the sensitivity of the differential thermometer. The latter effect is clearly significant and cannot be ignored.

(e) *Application of the above considerations to the ebullioscopic determination of molecular weights*

The foregoing discussion shows that when using temperature measuring devices other than the MENZIES differential thermometer, provided these are used differentially, the only effect which can have possible significance on the results is the variation of ebullioscopic constant with barometric pressure; this is best allowed for by correcting the ebullioscopic constant (or related apparatus constant) to standard atmospheric pressure using the correction terms c_1 given in Table I for the seven solvents listed, or, for other solvents, calculating the term as shown below.

On the other hand, when using a MENZIES differential thermometer all 4 effects may be significant, although under the conditions used by COLSON² it has been shown that only the 2 effects due to barometric pressure described in (c) and (d) are significant particularly the latter. However, COLSON ignores both these effects in his semi-micro method² and the former effect in his micro method; in the micro method the latter effect is allowed for by determining the boiling point to 0.1° with a mercury thermometer and, since a water-filled thermometer is used exclusively, by applying the appropriate factor¹. One way of allowing for all the above effects is to adopt a "bracketing" procedure such as that proposed by SWIETOSLAWSKI⁸ and adopted by KITSON *et al.*⁹, viz. to add alternately the standard reference compound and the sample in the same run, but this makes subsequent recovery of the sample difficult and assumes no interaction in solution; these objections do not apply to COLSON's methods, since the molecular weight of the sample is compared with that of the standard compound in separate runs.

To maintain the advantages of COLSON's methods, while at the same time obtaining consistent results in routine use, *i.e.* over periods when the barometric pressure may be expected to fluctuate over a wide range (*e.g.* 720–780 mm, as in the British Isles) it appears that the simplest procedure would be to apply a single correction, allowing for both pressure effects, which will convert the results obtained at the prevailing barometric pressure to standard atmospheric pressure; this solution is in any case obligatory when using a thermometer filled with a non-aqueous solvent (*e.g.* the benzene thermometer used in the extended semi-micro method³), since no tables exist for converting mm to °C in such cases and their compilation would be laborious. The derivation of the appropriate correction terms is accordingly given below, followed by their combination into a single comprehensive term.

DERIVATION OF THE CORRECTION TERMS

(a) *The correction term for the effect of variations in barometric pressure on the ebullioscopic constant K*

The required correction is for the rate of change of the ebullioscopic constant with

pressure at standard atmospheric pressure. This is obtained by eliminating the latent heat from (3.1) by using one of the approximate forms of the Clapeyron-Clausius equation⁷:

$$dp/dT = c_v p / RT^2 \quad (4.1)$$

c_v is the molar heat of vaporisation and is thus equal to $c_v M$, where M is the molecular weight of the solvent and c_v is the heat of vaporisation per g. Hence

$$K = pM/1000 \cdot dT/dp \quad (4.2)^*$$

the rate of change of the ebullioscopic constant with pressure, expressed as a percentage, is given by $100/K \cdot dK/dp$. Now

$$\begin{aligned} 100/K \cdot dK/dp &= 100/K \cdot dK/dT \cdot dT/dp \\ &= 10^5/pM \cdot dK/dT, \text{ substituting from (4.2)} \end{aligned} \quad (4.3)$$

if the vapour pressure-temperature relationship of the solvent is expressed by means of the Antoine equation¹³

$$\log_{10} p = A - B/(C + t) \quad (4.4)$$

where p is in mm Hg and t is in °C, differentiation gives

$$dt/dp = (C + t)^2 / 2.303 Bp \quad (4.5)^{**}$$

hence, since dT/dp and dt/dp are equivalent, substitution in (4.2) gives

$$K = M(C + t)^2 / 2303 B \quad (4.6)$$

which by differentiation gives

$$dK/dt = 2 M(C + t) / 2303 B \quad (4.7)$$

substitution for dK/dt ($\equiv dK/dT$) in (4.3) gives

$$100/K \cdot dK/dp = 86.9(C + t)/Bp \quad (4.8)$$

which reduces at the standard atmospheric pressure of 760 mm to

$$100/K \cdot dK/dp = 0.115(C + t)/B = c_1 \quad (4.9)$$

the correction term c_1 , *i.e.* the percentage change in ebullioscopic constant for 1 mm change in pressure at standard atmospheric pressure, is calculated in Table I for a representative range of ebullioscopic solvents. The Antoine constants given in the table for the non-aqueous solvents¹³ and water¹⁴ are suitably rounded off.

(4.2) has been derived from first principles by some authors^{10,11} and is indeed considered by ROY and FINK¹² to be preferable to (3.1) for calculating the ebullioscopic constant, since R, which they claim should be corrected by the Berthelot equation, has been eliminated.

This is differentiated erroneously as $\log_{10} C(C + t)^2/Bp$ by KITSON and MITCHELL⁵, presumably because of typographical confusion with $\log_{10} e(C + t)^2/Bp$.

TABLE I

CORRECTION TERM FOR THE EFFECT OF VARIATIONS IN BAROMETRIC PRESSURE ON THE EBULLIOSCOPIC CONSTANT

Solvent	Boiling point °C	Antoine constants		Correction term c_1 $= 0.115(C + t)/B$ %
		B	C	
Acetone	56.2	1233	230	0.0265
Carbon tetrachloride	76.7	1245	230	0.0282
Ethanol	78.3	1653	230	0.0214
Benzene	80.1	1206	220	0.0285
Water	100.0	1648	226	0.0226
Toluene	110.6	1344	219	0.0281
Chlorobenzene	131.7	1557	230	0.0266
Dioxan ^a	$T = 373^\circ\text{K}$	$B' = 1867$		0.023

^a Since the Antoine constants are not known for dioxan, the more approximate vapour pressure temperature relationship:

$$\log p = A' - B'/T \quad (\text{where } T \text{ is in } ^\circ\text{K}) \quad (4.1)$$

is used, leading to the analogous expression

$$100/K \cdot dK/dp = 0.115 T/B' \quad (4.1)$$

Although the correction term has been calculated at standard atmospheric pressure it may be used with negligible error for pressures in the vicinity of 1 atmosphere, e.g. for variations of ± 40 mm in pressure it can be shown from (4.8) that, by neglecting the slight change in t in comparison with the change in p , the correction term (which is itself small) varies by only $\pm 5\%$ of its value at standard atmospheric pressure. This conclusion can be reached more rigorously by differentiating (4.8) again with respect to pressure and expressing it as a percentage, viz.:

$$100 \cdot \frac{\frac{d}{dp} \left(\frac{86.9(C + t)}{Bp} \right)}{\frac{86.9(C + t)}{Bp}} = \frac{100}{p} \left(\frac{C + t}{2.303B} - 1 \right) \quad (4.1)$$

Substitution of the values for the Antoine constants and boiling point of, e.g., benzene gives a percentage change with pressure of -0.12% per mm in the percentage change of ebullioscopic constant with pressure, agreeing with the value of 5% per 40 mm obtained above.

The tabulated values, when converted from percentage to actual corrections, are slightly higher than those generally given in the tables of ebullioscopic constants to be found in the reference books, since the latter values are generally those calculated by HOYT AND FINK¹²; these authors neglect to take into account the variation of latent heat of vaporisation with temperature and their values are correspondingly slightly low. For example they give for carbon tetrachloride $K = 5.03^\circ$ per mole for 1000 g solvent with a barometric correction of 0.0013° per mm, whereas the correction term of 0.0282% per mm in Table I is equivalent to a correction of 0.0014° per mm. The difference caused by their error is obviously negligible for all practical purposes. The tabulated value for benzene agrees well with the value of 0.029% per mm for 760 mm derived from the ebullioscopic constants for benzene over the range 740–760 mm calculated recently from very accurate vapour pressure and thermal data.

b) *The correction term for the effect of variations in barometric pressure on the sensitivity of the Menzies differential thermometer*

The required correction is for the rate of change of thermometer sensitivity with pressure at the temperature corresponding to the boiling point of the given ebullioscopic solvent. This, expressed as a percentage of the sensitivity at that temperature, is equal to the product of the percentage rate of change of thermometer sensitivity per ° change in temperature at the boiling point of the ebullioscopic solvent and the rate of change of boiling point of the ebullioscopic solvent per 1 mm Hg change in pressure at atmospheric pressure, *viz.* $100d/(dt(d\bar{p})_f/(dt(d\bar{p})_f \cdot (dt/d\bar{p})_s)$, where the subscripts *f* and *s* denote the thermometer filling liquid and the ebullioscopic solvent respectively. By differentiating (4.5) this reduces to

$$200(C + t - 1.152B)/(C + t)^2 \cdot (dt/d\bar{p})_s = c_2 \quad (4.13)$$

where *B* and *C* are the Antoine constants of the filling liquid and *t* is the boiling point in °C of the ebullioscopic solvent; $(dt/d\bar{p})_s$ may be calculated from the Antoine constants of the ebullioscopic solvent using (4.5) or, more conveniently, may be taken from tables¹³.

Values of the correction term *c*₂ (*i.e.* the percentage change in thermometer sensitivity for 1 mm change in pressure at standard atmospheric pressure), calculated for the relevant thermometer filling liquids at the temperatures corresponding to the boiling-points of the ebullioscopic solvents used in the extension of COLSON's semi-micro method³, are given in Table II. Since 1.152*B* is greater than *C* + *t* the correction term is negative in sign, *i.e.* although the sensitivity (expressed as mm/°C) increases with increase in pressure (equivalent to increase in temperature), it decreases when expressed reciprocally as the Menzies factor in °/mm.

TABLE II

CORRECTION TERM FOR THE EFFECT OF VARIATIONS IN BAROMETRIC PRESSURE ON THE SENSITIVITY OF THE MENZIES DIFFERENTIAL THERMOMETER

Solvent	B.P. °C	$(dt/d\bar{p})_s$ at 760 mm Hg °C/mm	Benzene thermometer		Water thermometer	
			$(C + t - 1.152B)$	Correction term, <i>c</i> ₂	$(C + t - 1.152B)$	Correction term, <i>c</i> ₂
			$200 \frac{(C + t)^2}{\%}$	$\%$	$200 \frac{(C + t)^2}{\%}$	$\%$
Acetone	56.2	$3.80 \cdot 10^{-2}$	-2.92	-0.111	-4.07	-0.154
Carbon tetrachloride	76.7	$4.32 \cdot 10^{-2}$	-2.48	-0.107	-3.47	-0.150
Ethanol	78.3	$3.34 \cdot 10^{-2}$	-2.46	-0.082	-3.44	-0.115
Benzene	80.1	$4.27 \cdot 10^{-2}$	-2.42	-0.103	-3.38	-0.145
Dioxan	101.3	$4.32 \cdot 10^{-2}$	—	—	-2.95	-0.127
Toluene	110.6	$4.63 \cdot 10^{-2}$	—	—	-2.76	-0.128
Chlorobenzene	131.7	$4.88 \cdot 10^{-2}$	—	—	-2.52	-0.123

Although the tabulated values of the correction terms *c*₂ are strictly correct only at atmospheric pressure, they may be used without significant error over the range 720–780 mm. Thus the percentage change in *c*₂ with pressure is equal to the sum of the percentage changes with pressure in each of the terms $(dt/d\bar{p})_s$ and $200(C + t - 1.152B)/(C + t)^2$. These are found by differentiating with

respect to p to be respectively $100/p \cdot [(C + t)/1.152B - 1]$ and $43.4(C + t)/B \cdot [2.303B - (C + t)]/(C + t - 1.152B)$, reducing at atmospheric pressure to $0.13 [(C + t)/1.152B - 1]$ and $0.0572(C + t)/B \cdot [2.303B - (C + t)]/(C + t - 1.152B)$. Substitution for a typical set of conditions, *e.g.* benzene as ebullioscopic solvent with a benzene-filled thermometer, gives the percentage changes as respectively -0.103% per mm and -0.032% per mm; the total percentage change in c_2 with pressure is thus -0.135% per mm, this being due mainly to the change in dt/dp with pressure consequent upon the logarithmic form of the vapour pressure - temperature relationship for liquids. Thus for a change in pressure of 40 mm the percentage change in c_2 is 5.4% ; this is insignificant because c_2 itself is small. The same argument applies to all the solvent-filling liquid combinations examined.

(c) *Combination of the percentage correction terms c_1 and c_2 into a single comprehensive term*

Let the barometric pressure (corrected) = b mm Hg. Then, substituting in (3.5) and denoting the barometric pressure by subscripts,

$$\begin{aligned} \frac{K'_b}{K'_{760}} &= \frac{K_b}{K_{760}} \bigg/ \frac{f_b}{f_{760}} \\ &= \frac{1 + (b - 760)c_1/100}{1 + (b - 760)c_2/100} \\ &\approx 1 + (b - 760)(c_1 - c_2)/100, \text{ since } c_1 \text{ and } c_2 \text{ are both small.} \end{aligned} \quad (4.1)$$

Let $(c_1 - c_2)/100 = F$. Then if a mass m causes an elevation of boiling point ΔT , K' and K'_{760} can be replaced respectively by the proportional expressions $\Delta T/m$ (determined on a given ebulliometer at barometric pressure b mm) and Y (the value of $\Delta T/m$ corrected to standard atmospheric pressure), leading to

$$Y = \Delta T/m/[1 + F(b - 760)] \quad (4.2)$$

Values of F , calculated from the values of c_1 in Table I and c_2 in Table II, are collected in Table III. They are given to only 2 significant figures since the third figure is insignificant.

TABLE III

COMPREHENSIVE CORRECTION TERM FOR THE EFFECT OF VARIATIONS IN BAROMETRIC PRESSURE ON EBULLIOSCOPIC DETERMINATION OF MOLECULAR WEIGHT USING THE MENZIES DIFFERENTIAL THERMOMETER

Ebullioscopic solvent	F	
	Benzene thermometer	Water thermometer
Acetone	$1.4 \cdot 10^{-3}$	$1.8 \cdot 10^{-3}$
Carbon tetrachloride	$1.4 \cdot 10^{-3}$	$1.8 \cdot 10^{-3}$
Ethanol	$1.0 \cdot 10^{-3}$	$1.4 \cdot 10^{-3}$
Benzene	$1.3 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$
Dioxan	—	$1.5 \cdot 10^{-3}$
Toluene	—	$1.6 \cdot 10^{-3}$
Chlorobenzene	—	$1.5 \cdot 10^{-3}$

APPLICATION OF THE COMPREHENSIVE CORRECTION TERM IN THE EBULLIOSCOPIC DETERMINATION OF MOLECULAR WEIGHT

The determination of molecular weight by COLSON's methods² and the extension thereof³ simply consists of determining $\Delta T/m$ (in mm/mg) for both the sample and the standard compound in a fixed volume of an appropriate solvent, correcting these to the values Y at standard atmospheric pressure (using 4.15 and Table III), and, from the inverse relationship between Y and molecular weight, calculating the molecular weight of the sample, given the molecular weight of the standard.

For laboratories where the prevailing barometric pressure is much different from 760 mm, e.g. those at high altitudes, the necessary correction to standard atmospheric pressure to be applied may be 10% or more, and the approximations made in the above treatment leading to the values in Table III may become significant. It is then preferable to correct the results to a standard pressure other than 760 mm; this pressure should be the approximate mid-point of the pressure range encountered. Table III should then be recalculated using the equations developed above.

EXPERIMENTAL VERIFICATION OF THE COMPREHENSIVE CORRECTION TERM

The validity of the comprehensive correction term for the combination of benzene as ebullioscopic solvent with the benzene-filled differential thermometer was investigated by carrying out a series of 39 standardization experiments in a semi-micro ebulliometer; the solute was the standard compound benzil (mol. wt. 210) and the fixed volume of benzene was 10 ml. These experiments were performed at irregular intervals over a 12-month period at barometric pressures ranging from 717 to 778 mm Hg (over a range 751 mm Hg). The uncorrected values $\Delta T/m$ showed considerable scatter, with a range of 573 to 640 mm/g, a mean of 605 mm/g and a coefficient of variation of 2.3%, whereas the corrected values Y (using equation 4.15 with $F = 1.3 \cdot 10^{-3}$ from Table I) showed less scatter, with a range of 595 to 626 mm/g, a mean of 612 mm/g and a coefficient of variation of 1.3%. Further statistical analysis gave the following equations for the regression of respectively the uncorrected and corrected values on barometric pressure, where $\Delta T/m$ and Y are in mm/g and b in mm Hg:

a) *Uncorrected values*

Regression equation: $\Delta T/m = 605 + 0.744(b - 751)$. Standard error of the regression coefficient: 0.080. 95% confidence limits of the regression coefficient: 0.58 to 0.91.

b) *Corrected values*

Regression equation: $Y = 612 - 0.067(b - 751)$. Standard error of the regression coefficient: 0.081. 95% confidence limits of the regression coefficient: -0.23 to 0.10 . The analysis consequently shows that the dependence of the uncorrected values on pressure is highly significant, whereas that for the corrected values is not significant, thus verifying the validity of the comprehensive correction term.

ACKNOWLEDGEMENTS

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SUMMARY

A theoretical treatment of the effect of variations in barometric pressure and other factors on the ebullioscopic determination of molecular weights leads to general expressions relating the variation in barometric pressure with the ebullioscopic constant of the solvent and with the temperature sensitivity of the MENZIES differential thermometer. Since these variations can affect significantly the accuracy of ebullioscopic molecular weight determinations, a single comprehensive correction term is calculated for each of the usual combinations of ebullioscopic solvent and thermometer filling liquid; this term enables results obtained at different pressures to be corrected to standard atmospheric pressure, thus eliminating the pressure effect. Finally a statistical analysis of some experimental results illustrates the validity of the correction term for the combination of benzene as ebullioscopic solvent with benzene as thermometer filling liquid.

RÉSUMÉ

L'auteur a examiné l'influence des variations de la pression barométrique, ainsi que d'autres facteurs, sur la détermination des poids moléculaires par ébullioscopie (avec utilisation du thermomètre différentiel MENZIES).

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über den Einfluss des Luftdruckes sowie anderer Faktoren auf die ebullioskopische Molekulargewichtsbestimmung mit dem Differentialthermometer nach MENZIES.

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APPLICATION OF THE DOUBLE WITHDRAWAL COUNTERCURRENT EXTRACTION TECHNIQUE TO ANALYTICAL CHEMISTRY

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Although fractional solvent extraction and countercurrent distribution have been used for numerous chemical engineering processes, the use of the countercurrent distribution technique in chemical analysis has been primarily limited to what CRAIG classifies as the "fundamental" countercurrent extraction process¹. The "double withdrawal" process² would be of much greater interest and utility to the practicing analyst, but has unfortunately been largely neglected. Probably the major reason for its limited usage is the staggering complexity of the mathematics associated with the process. Before attempting to build an apparatus suitable for automatic operation, some knowledge of possible results from the use of the process is desirable. The manual performance of this extraction technique, with more than a few stages, is obviously out of the question.

A search of the literature has revealed only one attempt to solve the mathematics associated with the double withdrawal countercurrent extraction process. COMPERE AND RYLAND³ attacked the problem through the probability concept of the random walk and presented results calculated for several cases. However, this method of calculation is quite difficult and is an obstacle of sufficient prominence to prevent consideration of the method in the laboratory.

The writer preferred to attack the problem by means of present day computer technology so that results could be obtained rapidly for several conditions in order to determine whether or not the process was of analytical interest. Although the double withdrawal process has been described elsewhere^{2,3}, a brief description here seems advisable in order to clarify the terms to be used.

The double withdrawal extraction pattern is shown in Fig. 1 and is similar to that shown by COMPERE AND RYLAND. Each circle represents an extraction container, such as a separatory funnel. For purposes of simplicity, we shall consider what happens to only one material. The material under consideration is fed into the first container (C) as indicated and the solvent volumes are adjusted so that there are equal volumes of each phase. For simplicity of treatment, all phase ratios will be adjusted to unity. The mixture is shaken and allowed to separate. The heavy phase is drained and transferred to tube R₁ as indicated, and the light phase is transferred to tube L₁. This is called the first extraction, or $n = 1$. Heavy solvent is added to tube L₁ and light solvent is added to tube R₁. These two mixtures are shaken and allowed to separate. The heavy solvent in L₁ is transferred to C and the light solvent in L₁ is transferred to L₂. Similarly, the heavy solvent in R₁ is transferred to R₂ and the light solvent

transferred to C. This is the second extraction, or $n = 2$. Heavy and light solvents are added to L2 and R2 respectively and the three mixtures are shaken and allowed to separate. The heavy solvent in R2 and light solvent in L2 are withdrawn as product. The heavy solvents in C and L2 are transferred to R1 and L1 respectively. The light solvents in C and R2 are transferred to L1 and R1 respectively. This is the third extraction, or $n = 3$. This procedure is carried on for any number of extractions desired. It will be noticed that light and heavy products are obtained after every other extraction, and that appropriate solvent must be added as indicated. The system shown in Fig. 1 is considered as having five stages ($S = 5$). It can be shown that the

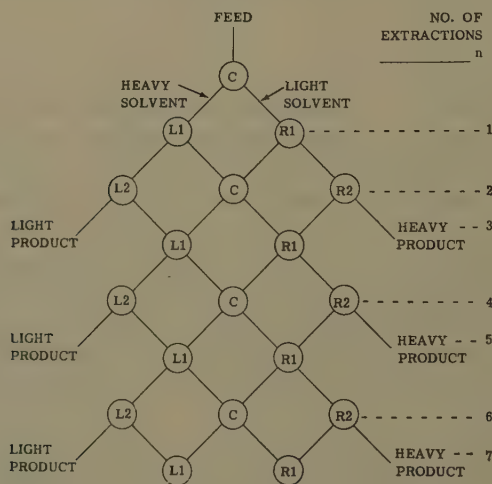


Fig. 1. Double withdrawal extraction pattern.

first portion of product is obtained after $(S + 1)/2$ extractions, where S designates the number of stages. If we assume that the fraction of the material transferred to the heavy solvent after one extraction is α , and the fraction transferred to the light solvent is β it can be shown that for five stages, the total amount of material collected in the heavy solvent product after 3 extractions is α^3 , after 5 extractions it is $\alpha^3 + 3\alpha^4\beta$, after 7 extractions it is $\alpha^3 + 3\alpha^4\beta + 9\alpha^5\beta^2$, etc. It can also be shown that the total amount collected (again considering only the heavy solvent product) may be represented by

$$Q = M(A\alpha^r + B\alpha^{r+1}\beta + C\alpha^{r+2}\beta^2 + D\alpha^{r+3}\beta^3 + \dots)$$

where S = number of stages, $r = (S + 1)/2$, Q = total amount of material collected, M = amount of material originally present, α = weight fraction of material extracted into heavy solvent in one extraction, β = weight fraction of material extracted into light solvent in one extraction, and $\alpha + \beta = 1$. A, B, C, D , etc., are coefficients. The number of coefficients to be used and the value of each coefficient is determined by the number of stages and the number of extractions performed. Initially, it would appear that some simple relationship exists for these coefficients. For example, for $S = 5$ the values of the coefficients are 1, 3, 9, 27, 81, etc. For $S = 3$, the values are 1, 2, 4, 8, 16, 32, 64, etc. Thus, for 3 or 5 stages, the coefficients are a function of $[(S + 1)/2]^r$.

However, when $S = 7$, the values for these coefficients are 1, 4, 14, 48, 164, 560, etc. Likewise, for $S = 9$, the coefficients are 1, 5, 20, 75, 275, 1000, etc., for $S = 11$, the coefficients are 1, 6, 27, 110, 429, etc. A careful examination of these coefficients has led to the conclusion that no simple relationship exists between them.

It therefore seemed appropriate to use the International Business Machine 704 computer to solve for and store coefficient values for different combinations of S and n . This was done for odd values of S from 3 through 101; also for $S = 111, 121, 131, 141, 151, 161, 171, 181, 191, 201, 221, 241, 261, 281, 301, 351, 401, 501, 601, 701, 801$, and 1001. Coefficients were obtained for each of the preceding values of S for up to 100 extractions, or until the machine could no longer handle the data. To indicate the order of magnitude of some of the coefficients, values of 10^{140} are not uncommon.

After the coefficients had been stored, the total products for values of $\alpha = 0.01, 0.02, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 0.95, 0.98$, and 0.99 were obtained for a number of different stages and extractions. The machine carried on the problem solution until essentially all of the material was removed from the system, or until the machine limitations were reached. The computer was programmed to stop before giving incorrect answers. The computer program used in this work is indicated later.

The information obtained is shown plotted in Figs. 2-9 as total percent extracted

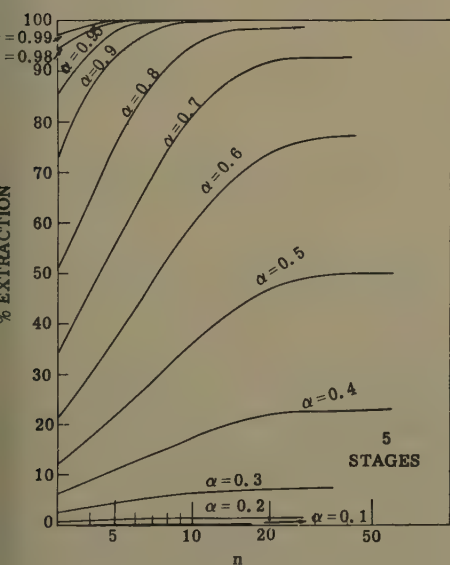


Fig. 2. Theoretical double withdrawal recoveries with 5 stages.

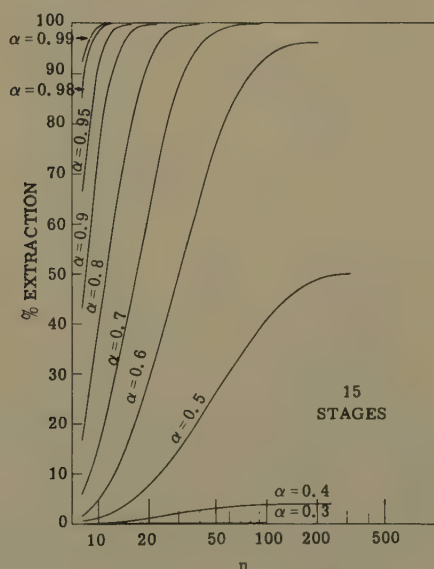


Fig. 3. Theoretical double withdrawal recoveries with 15 stages.

for various values of α) vs. the number of extractions. Several points should be remembered while considering these curves. First, in a separation of two materials, x and y , where for example, $\alpha_x = 0.9$ and $\alpha_y = 0.7$, the material having a value of $\alpha = 0.9$ will appear first in the product. Assuming that the separation is done automatically and that there are both kinds of solvent in all the tubes, solvent will be collected containing separated material on alternate values of n . Note that separated

material is not obtained until $(S + 1)/2$ extractions, therefore the material has been diluted much less than it would seem.

The amount extracted for values of α not shown in the figures is essentially zero.

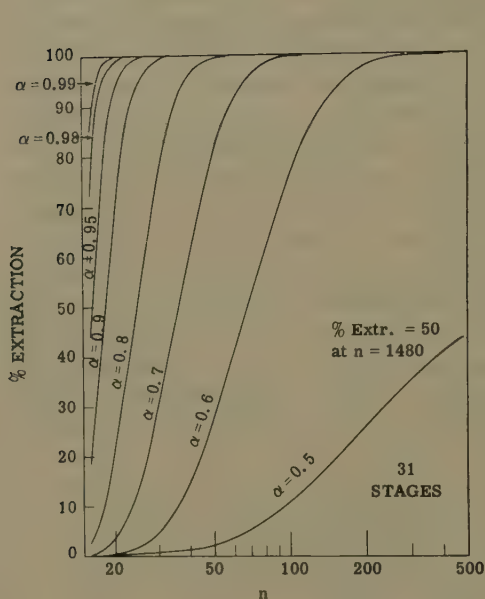


Fig. 4. Theoretical double withdrawal recoveries with 31 stages.

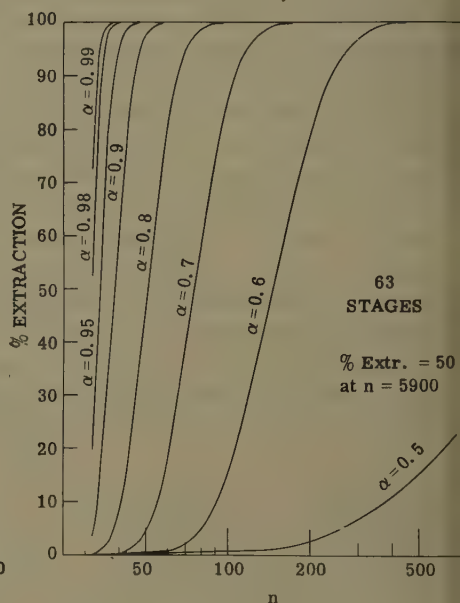


Fig. 5. Theoretical double withdrawal recoveries with 63 stages.

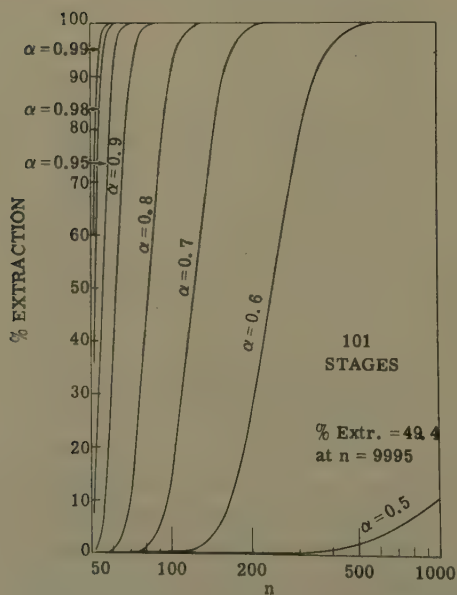


Fig. 6. Theoretical double withdrawal recoveries with 101 stages.

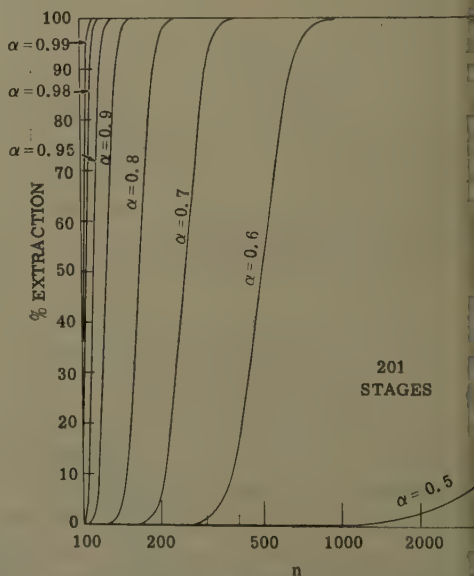


Fig. 7. Theoretical double withdrawal recoveries with 201 stages.

for the range of extractions covered. It should be noted that only the material obtained in the heavy solvent product is considered. (The amount collected in the light product will of course be the same as that collected in the heavy product for $1 - \alpha$).

Examination of Figs. 2-9 indicates that the double withdrawal process has some very interesting analytical possibilities. To illustrate the advantage of this procedure over the direct extraction technique, let us compare the separation of two substances, x and y , where $\alpha_x = 0.9$ and $\alpha_y = 0.3$. If we start with equal amounts of x and y , and a phase ratio of unity, after one extraction using the direct extraction technique, the amounts of x and y in the extract would be 90% and 30% of the original amount

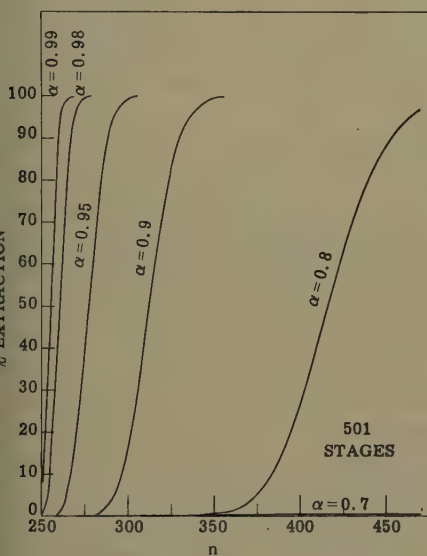


Fig. 8. Theoretical double withdrawal recoveries with 501 stages.

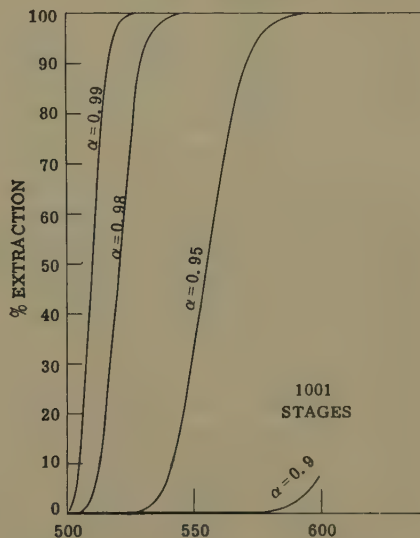


Fig. 9. Theoretical double withdrawal recoveries with 1001 stages.

respectively. If we desire for analytical purposes to recover at least 99% of the amount initially present, another extraction must be made of the original phase which contained the material to be separated. This time we obtain 9% of material x (90% of 90%), and 21% of material y (30% of 70%). We now have recovered 99% of x and the purity of our material (with respect to x) has improved from an original 50% to 66%. Table I indicates recovery and purity data for the separation of x and y for two different cases. Note that as the percent recovery increases, the purity decreases.

TABLE I
RECOVERY AND PURITY BY DIRECT EXTRACTION TECHNIQUE

n	$\alpha_x = 0.9; \alpha_y = 0.3$		$\alpha_x = 0.9; \alpha_y = 0.7$	
	% Recovery (x)	% Purity (x)	% Recovery (x)	% Purity (x)
1	90	75	90	56.2
2	99	66	99	52.1
3	99.9	60.5	99.9	51.6
4	99.99	56.8	99.99	51.2

It is obvious from Table I that the direct extraction technique is relatively useful for analytical separations unless the distribution coefficients of the materials to be separated are considerably different.

In contrast to the direct extraction technique, Fig. 3 indicates that after 22 extractions using the countercurrent technique and 15 stages, 99.9% of x would be recovered essentially 99.9% pure when $\alpha_x = 0.9$ and $\alpha_y = 0.3$. If we assume a volume of 10 ml for each phase, the total amount of solvent which contained material x would be $(220 - 80)/2$ or 70 ml.

Fig. 7 indicates that after 155 extractions with 201 stages, 99.9% of x is again recovered essentially 99.9% pure when $\alpha_x = 0.9$ and $\alpha_y = 0.7$. Note that the volume containing x is $(1550 - 1000)/2$ or 275 ml, again assuming initial phase volumes of 10 ml. Furthermore, lest 201 stages seems to be of theoretical value only, the reader is referred to the work of CRAIG in which 1000-cell countercurrent distribution instruments have been used for automatic separations.

Figs. 2-9 are obviously not all-inclusive; the values of α and S were selected to give a reasonable amount of information and still meet the usual space requirements. Careful examination of the figures will indicate the applicability of the double withdrawal countercurrent technique to chemical analysis. In Fig. 2 for example, quantitative recovery (99.9%) is obtained, using 5 stages, only for material having α equal to or greater than approximately 0.9. For lower values of α , somewhat less than 100% recovery is obtained (in the heavy solvent product); the remainder of the material is obtained in the light solvent product. The figures have been drawn to indicate either essentially complete removal of material from the system, or to indicate computer limitations. When the curve asymptotically approaches the horizontal, one may assume complete removal from the system. The curves shown in Fig. 2 also indicate that a quantitative separation of material having α equal to (or greater than) 0.9 is obtained only from material having α equal to approximately 0.1 to 0.2 (depending upon exactly what is meant by the word quantitative). The curves in Figs. 3-9 can be interpreted in the same manner.

Examination of the figures indicates the possible separations which might be made depending upon the distribution coefficients involved. The closer the distribution coefficients of the materials to be separated are to each other, the greater the number of stages needed for extraction. It is quite interesting to note however, that the material desired will be collected in a volume which will not prohibit use of the usual analytical methods.

The following assumptions are of course implicit in the foregoing treatment:

1. The distribution coefficients are independent of concentration.
2. Equilibrium is assumed to have occurred for each extraction.
3. Complete separation and transfer of the phases occurs with no solvent loss or evaporation.
4. The phases are immiscible, or can be pre-equilibrated.
5. No chemical interaction or phase inversion occurs.

The foregoing data have indicated the application of the double withdrawal countercurrent extraction technique to chemical analysis. Work is proceeding to test this type of separation experimentally, the final objective being the development of an automatic apparatus. It is hoped that this article will stimulate sufficient interest among analysts to warrant other experimental investigations.

COMPUTER PROGRAM

For persons interested in obtaining results not included in this report, a program has been written for the International Business Machine 704 computer which will compute, for a given number of stages, either (1), the coefficients A, B, C, D, \dots or (2), for a given value of α , the quantity Q collected in either solvent product as a function of A, B, C, D, \dots on the assumption of a unit mass originally introduced into the middle stage. In both cases the coefficients A, B, C, D, \dots are generated by the following scheme, shown for illustrative purposes with 13 stages:

I	I	I	I	I	I	I	0
2	3	4	5	6	7	7	0
6	10	15	21	28	35	35	0
20	35	56	84	119	154	154	0
70	126	210	329	483	637	637	0
252	462	791	1274	1911	2548	2548	0
924	1715	2989	4900	7448	9996	9996	0
.....

The first column corresponds to the middle (7th) stage and the second column from the right contains the coefficients A, B, C, D, \dots . If $\gamma_{i,j}$ denotes the number in the i -th row and j -th column, the $\gamma_{i,j}$'s are generated recursively as follows:

$$\gamma_{1,j} = 1 (j = 1, 2, \dots, r); \gamma_{1,r+1} = 0$$

$$\gamma_{i,1} = 2\gamma_{i-1,2} (i = 2, 3, \dots)$$

$$\gamma_{i,j} = \gamma_{i,j-1} + \gamma_{i-1,j+1} (j = 2, 3, \dots, r; i = 2, 3, \dots)$$

Hence

$$\gamma_{1,r} = A, \gamma_{2,r} = B, \gamma_{3,r} = C, \text{ etc.};$$

In the example,

$$\gamma_{1,7} = A = 1, \gamma_{2,7} = B = 7, \gamma_{3,7} = C = 35, \text{ etc.}$$

Since a number equal to or greater than 2^{128} cannot be represented in the computer, the rows occurring in this generation scheme may need to be scaled several times to keep the numbers within the proper range. (When printed out, the coefficients A, B, C, D, \dots and the quantities Q are rescaled). However, if the ratio $\gamma_{i,r}/\gamma_{i,1}$ ever exceeds 2^{128} , as may happen with large values of S , the machine limitations are exceeded and the computations cease. Results so far indicate that this condition will occur for values of S greater than about 300. This does not mean that the program is not valid for values of S greater than 300; it only indicates that one might not be able to obtain as many coefficients or extractions as is desired. This is especially true for S much greater than 300 or for α near to 0.5. With this exception, a specified number of coefficients or extraction quantities may be computed for any value of S . The computer may be asked to stop computations after a specified percent recovery.

More explicit directions will be supplied if the program itself is requested.

ACKNOWLEDGEMENTS

The author gratefully acknowledges the assistance of R. G. HERRMANN who program-

med the International Business Machine 704 computer and obtained the numeric results which are the basis for this presentation. The author feels considerably indebted to J. A. MCGURTY for his support of this program and to H. S. EDWARDS for his recommendations concerning presentation.

SUMMARY

Application of the double withdrawal countercurrent extraction technique to chemical analysis has been singularly neglected, probably because of the complexity and tediousness of the associated mathematics. Present day computer technology proved to be readily applicable to the problem and information is presented which indicates the possible importance of this separation method to chemical analysis.

RÉSUMÉ

L'auteur décrit l'emploi d'un "computer" pour le traitement mathématique des procédés d'extraction à contrecourant, avec double prélèvement. Il démontre l'importance de ce procédé pour l'analyse chimique.

ZUSAMMENFASSUNG

Es wird über die Anwendung der "Computer" zur mathematischen Behandlung des Gegenstrom-Extraktionsverfahrens mit doppelter Entnahme berichtet. Auf die Bedeutung des Verfahrens für chemische Analysen wird hingewiesen.

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TITRIMETRIC METHODS FOR THE MICRODETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS BY THE RAPID COMBUSTION PROCEDURE

I. THE DETERMINATION OF INDIVIDUAL HALOGENS

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INTRODUCTION

Several titration procedures for the microdetermination of the halogens (chlorine, bromine and iodine) in organic compounds were outlined in the original communication to this journal on the rapid, empty tube combustion procedure¹. In a more recent paper, INGRAM² has suggested that for daily routine analysis potentiometric titration is preferable to other titration procedures for the evaluation of the halogens. However, it may not always be convenient to use this method, and if non-instrumental methods are equal in speed and accuracy they are generally to be preferred. Other acid-producing elements, such as nitrogen and sulphur, which often occur in organic combination with one or more of the halogens, can influence considerably the type of absorbent required for a particular halogen. The choice of the final titrimetric procedure is influenced by the absorbent used.

Because several important aspects of these methods were not fully discussed in the earlier publications¹⁻³, it is proposed to present a short series of papers describing the results of later experience and of a study⁴ on various titrimetric procedures suitable for the microdetermination of the halogens in all their possible organic combinations with oxygen, nitrogen, sulphur and with each other.

DISCUSSION

halogens in the absence of nitrogen and sulphur

The combustion products from these halogenated organic compounds consist almost exclusively of carbon dioxide, water vapour and the free halogen. It is unlikely that hydrogen halides can be formed, for at the elevated temperatures of this combustion complete oxidation is to be expected. Chlorine and bromine were originally absorbed in neutral hydrogen peroxide which allowed a direct acidimetric titration to be used. The reactions of iodine with hydrogen peroxide are, however, too complex to be dependable, and absorption in strong alkali or bisulphite or both is generally preferred.

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Halogens in the presence of nitrogen

The mechanisms involved in the destructive oxidation of nitrogenous substance by the rapid combustion method have not been fully elucidated. INGRAM⁵ has shown that in addition to the free halogen, water vapour and carbon dioxide, both elemental nitrogen and oxides of nitrogen are produced in varying amounts depending on the nature of the original nitrogen linkage. Calculations from available thermodynamic data indicate that the prevailing conditions do not favour any appreciable additional oxidation of the elemental nitrogen to nitric oxide⁴. INGRAM found that most types of nitrogenous compound produce relatively small amounts of nitric acid when the combustion products are absorbed in a neutral hydrogen peroxide solution, but nitrogen compounds, not unexpectedly, give a high rate of conversion to nitrogen dioxide. In most cases the quantity of nitric acid formed prevents the direct acidimetric titration of the halogen acid.

Halogens in the presence of sulphur

When organic compounds containing sulphur are burned, the experimental evidence suggests that the sulphur is converted initially to sulphur dioxide. It is most unlikely that further oxidation of the sulphur dioxide to the trioxide would occur; it is well established that sulphur trioxide undergoes dissociation to the dioxide very readily at moderately high temperatures. At the cooler exit-end of the combustion tube, however, conditions favour oxidation to the trioxide; unless the outlet is kept warm, appreciable condensation of sulphuric acid occurs at this point.

It is also possible under the prevailing conditions for chlorine and sulphur dioxide to react to yield sulphuric acid and hydrogen chloride^{4,6}. When the products of combustion from various sulphur- and chlorine-containing compounds were collected in a liquid air trap and examined in the mass spectrometer it was found that β -sulphur trioxide was present in addition to carbon dioxide, sulphur dioxide and water⁴. No trace of any gaseous halogen derivative was found, but when the sulphur trioxide was dissolved in hydrogen peroxide, chloride ion was detected (84% of the original amount)⁴. Evidently this material had absorbed the hydrogen chloride⁷. No sulphur chloride or chlorosulphonic acid was found.

Conclusions on the composition of the breakdown products

The principal products are carbon dioxide, water vapour, the free halogens and depending upon the original elemental composition of the compound, variable quantities of nitrogen, oxides of nitrogen and sulphur, nitric and sulphuric acids and hydrogen chloride. It is extremely unlikely that hydrogen bromide or iodide are formed in the gaseous state.

When the absorption media and titration procedures for the halogens are selected all the possible combustion products must be considered.

Some possible titrimetric methods for the halogens

Argentometric titrations have only been successfully applied to the microdetermination of the halogens by the rapid method when the end-point is detected potentiometrically. The mercuric oxycyanide method of VIEBÖCK⁸ as modified by BELCHER⁹ MACDONALD AND NUTTEN⁹ has been found to be the most widely applicable visu-

micro titration for the halogens; nitric and sulphuric acids do not interfere. Owing to the less favourable conversion factors, the titration of bromide or iodide is more exacting than that of chloride but, with care, results within the usual limits of accuracy can be obtained.

The most sensitive methods for the halogens are the amplification procedures which are based on the oxidation of the halide to the corresponding halate followed by an iodometric evaluation of the latter. Both the LEIPERT micro method¹⁰ for iodine and the hypochlorite oxidation method of KOLTHOFF AND YUTZY¹¹ for bromine were found to give satisfactory results. Several indirect amplification procedures for chloride ions were examined by BELCHER AND GOULDEN¹², but they concluded that none was sufficiently accurate for microdeterminations.

The combustion products of bromine or chlorine compounds which do not contain nitrogen or sulphur can be absorbed in hydrogen peroxide solutions so that the halogen can be determined by an acidimetric titration.

Hydrogen peroxide solution as absorbent

The reaction kinetics of halogens with hydrogen peroxide have been studied extensively^{4,13}. The reactions with bromine and chlorine are similar, each halogen being reduced to the corresponding halide under the conditions used. The reactions of iodine with peroxide depend on the medium^{4,14,15}: in acid solution an almost quantitative oxidation to iodate occurs, but in alkaline solution there is complete reduction to iodide. In our attempts to exploit this reaction we were able to show that iodide ions were formed quantitatively during the alkaline peroxide absorption, but the iodide values obtained by direct acidimetric titration were very variable⁴. Hence, this titration procedure cannot be recommended for the determination of iodine.

Neutral hydrogen peroxide is usually a satisfactory absorbent for chlorine and bromine but it is less efficient than alkaline peroxide in the rapid combustion method; when compounds containing large amounts of bromine and, to a smaller extent, chlorine, are burnt, some slip occurs with neutral solutions. It is recommended, therefore, that alkaline hydrogen peroxide solutions always be used.

Alkaline bisulphite solution as absorbent

This solution can be used for the absorption of all three halogens. When two or more halogens are present it is to be preferred to hydrogen peroxide which may initiate a series of interfering side reactions⁴. However, alkaline peroxide is preferable when only one halogen has to be absorbed and the mercuric oxycyanide titration is used; hydrogen peroxide need not be removed whereas sulphur dioxide must be completely expelled.

Absorption of iodine

It was stated earlier that when alkaline hydrogen peroxide is used for absorption of iodine, direct acidimetric titration is not possible. The mercuric oxycyanide procedure can be applied since iodide is formed quantitatively, but the LEIPERT method is to be preferred. With the former method great care is necessary in the titration because of the unfavourable conversion factor; even when sample weights of 8–12 mg are used, the titrant must be measured to ± 0.015 ml to obtain the required accuracy. This procedure only finds application in the special case where the other halogens

are present and their total amount has to be determined; the experimental details are exactly the same as for the determination of chlorine and bromine with the important exception that hydrogen peroxide must be completely destroyed (by means of a platinum-black destructor rod) before acidification.

The well-known LEIPERT procedure with its six-fold amplification should be applied whenever possible. INGRAM recommended an acetic acid-sodium acetate buffer solution of bromine as absorbent³. We prefer sodium hydroxide solution for this purpose to avoid the bromine fumes; it is important, however, to avoid high electrolyte concentrations which decrease the sensitivity of the starch end-point. We also prefer phosphoric to acetic acid for neutralising the excess of alkali; it is not then necessary to add acetic acid-sodium acetate buffer because the solution is buffered sufficiently by the sodium phosphate produced in the neutralisation. The total electrolyte concentration is thus reduced to about one-half of the usual amount.

EXPERIMENTAL

A. Determination of chlorine or bromine (in absence of N and S)

Indicators

(1) Screened methyl red-methylene blue indicator solution. Prepare separate solutions of 0.125 g of methyl red in 50 ml of 90% ethanol and 0.083 g of methylene blue (redox purity) in 50 ml of 90% ethanol, and mix equal volumes of the two solutions immediately before use. (2) Aqueous methyl red indicator solution.

Procedure

Burn the sample as described in the earlier paper¹ using as absorption solution an exactly measured volume of 0.01 *N* sodium hydroxide (*ca.* 10 ml), together with a known volume of 30% hydrogen peroxide (0.5–1.0 ml) on which a deduction may be required for its alkali blank.

After the combustion is complete, run the contents of the absorber into a 100-ml conical flask, and rinse the absorber, and the outlet wash tube from the combustion tube, 2–3 times with 3–5-ml portions of neutral distilled water. Add a known excess of 0.01 *N* sulphuric acid and a few drops of aqueous methyl red indicator, boil gently for 2–3 min, cool and then back-titrate with 0.01 *N* sodium hydroxide, after the addition of 8–10 drops of the screened indicator solution.

1 ml of 0.01 *N* NaOH \equiv 0.3546 mg Cl or 0.7992 mg Br

B. Determination of chlorine (in presence of S and/or N)

Saturated mercuric oxycyanide solution

Shake 20 g of mercuric oxycyanide with 1 l of distilled water and set aside overnight. Filter this stock solution into a brown glass bottle and store away from strong light.

Procedure

Carry out the combustion, absorption and final titration with 0.01 *N* sodium hydroxide as described for A, but match the end-point of the titration against an equal volume of neutral distilled water and screened indicator solution contained in a second matched 100-ml conical flask. Add 10 ml of the stock mercuric oxycyanide

ution to the first flask and titrate the hydroxyl ions liberated with 0.01 *N* sulphuric acid until the colours of the two solutions again match. Add the same volume of 0.01 *N* sulphuric acid to the contents of the second flask together with 10 ml of mercuric cyanide solution and titrate with 0.01 *N* sodium chloride until its colour reaches that of the first flask.

The chloride content of the original absorption solution \equiv volume of 0.01 *N* sodium chloride consumed, *i.e.*

$$1 \text{ ml of } 0.01 \text{ } N \text{ NaCl} \equiv 0.3546 \text{ mg Cl}$$

C. Determination of bromine (in presence of S and/or N)

Method 1

Neutral mercuric oxycyanide solution. Carefully neutralise the stock solution with 0.1 *N* sulphuric acid in the presence of a few drops of methyl red/methylene blue greened indicator.

Procedure. Carry out the combustion, absorption and titration with 0.01 *N* sodium hydroxide as in *A, B*. Add to the neutralised absorption solution 10 ml of the neutral mercuric oxycyanide solution and titrate the released hydroxyl ions very carefully with 0.01 *N* sulphuric acid until a faint pink tinge is reached. A compensation titration not necessary for bromide⁹.

$$1 \text{ ml of } 0.01 \text{ } N \text{ H}_2\text{SO}_4 \equiv 0.7992 \text{ mg Br}$$

Method 2 (based on method of Kolthoff and Yutzy¹¹)

Reagents (a) 5% Aqueous sodium hypochlorite solution: 90 ml of 14–15% bromine-saturated sodium hypochlorite solution diluted to 250 ml with distilled water.

(b) 50% Sodium formate solution: 32 ml of formic acid added slowly with cooling to 30 g of sodium hydroxide dissolved in a little water and finally diluted to 100 ml with distilled water.

(c) 5% Aqueous ammonium molybdate solution.

Procedure. In this case, the halogen is best absorbed in fairly strong alkali, hence it is advisable to reserve a separate absorber because alkali tends to adsorb on the glass surface and interferes with later acidimetric determinations.

Charge the bead-filled absorber with a mixture of 6–8 ml of 1 *N* sodium hydroxide solution and 5–6 drops of 35% bisulphite solution. Burn the sample as usual and transfer the resulting absorption solution, together with the aqueous washings from the absorber, to a 250-ml stoppered, conical flask; heat to boiling for a couple of minutes with 2–3 drops of 30% MAR hydrogen peroxide. Cool the contents of the flask quickly to room temperature and neutralise with 1 *N* phosphoric acid using aqueous methyl red as indicator. Add 5 ml of 5% hypochlorite solution, cover the flask with watch glass and heat the solution slowly almost to boiling over a period of 8–10 min. Remove the flask from the source of heat, wash down its wall with a little distilled water and add 5 ml of 50% sodium formate solution. Mix the contents of the flask thoroughly by frequent swirling to ensure the complete destruction of the excess of hypochlorite solution. When the bromate solution has reached room temperature, add 5 ml of 9 *N* sulphuric acid, followed by 1–2 drops of 5% ammonium molybdate and ca. 0.5 g of solid potassium iodide. Stopper the flask, mix well and set aside for 10 min. Titrate the released iodine with 0.02 *N* sodium thiosulphate solution, adding small quantity of Thyodene indicator just before the end-point is reached.

It is essential to carry out a blank determination on all the reagents, preferably by the combustion of a non-halogenated sample such as benzoic acid as a check on the absorption solution.

$$1 \text{ ml of } 0.02 \text{ N Na}_2\text{S}_2\text{O}_3 \equiv 0.26639 \text{ mg Br}$$

D. Determination of iodine (in the presence or absence of S and/or N)

Procedure

Charge the bead-filled absorber with 6–7 ml of 1 N sodium hydroxide and burn the sample as usual. Transfer the alkaline absorption solution to a 250-ml stoppered conical flask and wash the absorber thoroughly with water ($3 \times 3\text{--}5\text{-ml}$ portions). Neutralise the contents of the flask with 1 N phosphoric acid in the presence of a few drops of aqueous methyl red indicator solution. Then add 1.0–1.5 ml of saturated bromine water and allow the mixture to stand stoppered for 5 min. Destroy the excess of bromine by the dropwise addition of formic acid and test for complete removal of bromine with aqueous methyl red indicator. Add 5 ml of 2 N sulphuric acid and 0.5 g of solid potassium iodide and titrate the released iodine 2 min later with 0.02 N sodium thiosulphate in the usual way.

$$1 \text{ ml of } 0.02 \text{ N Na}_2\text{S}_2\text{O}_3 \equiv 0.4231 \text{ mg I}$$

ADDENDUM

Since the above work was completed, an interesting modification of the mercurimetric titration of chloride has been described by CHENG¹⁶ who applied it after the oxygen flask method of decomposition of the organic material. The titration is done with 0.01 N mercuric nitrate solution in the presence of diphenylcarbazone indicator¹⁷ but sufficient ethanol or isopropanol is added to give an approximately 80% alcohol medium. This not only effects a startling improvement in the sharpness and clarity of the end-point but also achieves a more stoichiometric relationship.

The usual titration in aqueous media is unattractive on the microscale, for the end-point is indistinct. On any scale of working the titration is not stoichiometric and the reactions which occur appear to be complicated; probably a slight dissociation of the mercuric chloride complex, HgCl_2 , is partly compensated by a tendency to form less stable mercury chloride complexes¹⁸ such as HgCl^+ . In any case it is advisable to standardise the titrant under the conditions of the actual determination.

CHENG used the method for bromine and chlorine determinations, taking sufficient sample to provide 1–1.5 mg of halogen, and standardised the titrant under the same conditions. We have found that a wider range is possible if the volume of solution used by CHENG is halved, *i.e.* if 10 ml of aqueous solution and 40 ml of ethanol are used. This procedure is suitable for 1–2 mg of halide, the titrant being standardised again with an appropriate amount of alkali halide under similar conditions. Different 1-mg ranges can be used (up to 5 mg of chloride) so long as the titrant is standardised within the range taken. The method is not suitable for semimicro work.

This technique can profitably replace the mercuric oxycyanide method described above for all individual chlorine and bromine determinations; it is not suitable for iodine determinations or for mixed halogen determinations, hence the mercuric oxycyanide method is still retained for general purposes. Combustion and absorption a

carried out as described above in Procedure A. The inlet wash tube is rinsed with 1–2 ml of water and the absorber is detached and rinsed thoroughly with ethanol, 40 ml of which are added altogether. The solution is then neutralised with 0.05 *N* nitric acid and the determination completed as described by CHENG¹⁶. It is not necessary to remove hydrogen peroxide.

This procedure is also excellent after decomposition by the oxygen flask technique. Our present routine practice is to use the flask method except for highly volatile liquids or refractory compounds where the empty tube method has proved to give more reliable results.

ACKNOWLEDGEMENT

We are grateful to Professor R. BELCHER for his helpful advice and guidance in this work.

SUMMARY

A critical study has been carried out of titrimetric methods suitable for the microdetermination of each of the halogens, chlorine, bromine and iodine, in their possible organic combinations with the elements, oxygen, nitrogen and sulphur, following organic decomposition by the rapid empty tube combustion procedure.

RÉSUMÉ

Une étude critique a été effectuée sur les méthodes titrimétriques, utilisées pour le microdosage des halogènes (chlore, brome, iode) dans les substances organiques.

ZUSAMMENFASSUNG

Beschreibung einer kritischen Untersuchung über die Titrationsmethoden zur Mikrobestimmung von Chlor, Brom und Jod in organischen Substanzen.

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KINETICS OF DECOMPOSITION OF YTTRIUM, CEROUS AND ZIRCONYL OXALATES

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INTRODUCTION

Thermogravimetric and differential thermal analysis are used to study solid state decomposition reactions at high temperatures. The temperature of decomposition of some of the oxalates of lanthanides have been recently studied thermogravimetrically but the kinetics of decomposition has not been calculated. This paper reports the rate-dependent parameters of the decomposition of yttrium, cerous and zirconyl oxalates according to the methods of FREEMAN AND CARROLL¹, and BORCHARDT AND DANIELS².

EXPERIMENTAL

Yttrium oxalate and cerous oxalate were prepared from the respective nitrates (E. Mercks) by the method reported by WENDLANDT³. Zirconyl oxalate was prepared from its chloride (E. Mercks) according to TAKAGI⁴.

A Stanton thermobalance (high temperature model) was used for the thermogravimetric measurements. The rate of heating was maintained at about 6°/min. Weight losses were within 2% of the theoretical values.

The apparatus for DTA was designed in this laboratory. Two platinum cells 8 mm in diameter and 15 mm high, with a capacity of 700 mg of tightly packed alumina were used. The heating was controlled by a Honeywell-Brown programme controller recorder, and the differential temperature was recorded by a differential mV recorder. The rate of heating was maintained at 5°/min.

For DTA study, the sample was well mixed with extra pure alumina (E. Merck) and tightly packed in one cell whereas alumina alone as reference material was taken in the other.

RESULTS AND DISCUSSIONS

Yttrium oxalate

The analysis of the compound prepared for the present work corresponded to $Y_2(C_2O_4)_3 \cdot 9 H_2O$. The thermogram (Fig. 1) showed that the water of hydration began to evolve at 60° and continued up to 200°. After this the curve became horizontal to the time and temperature axis with a constant weight region between 200°–260° corresponding to $Y_2(C_2O_4)_3 \cdot 2 H_2O$. The dihydrate started decomposing at 260°. There was a break in the curve at 415°, the temperature at which the anhydrous $Y_2(C_2O_4)_3$ was obtained. Its decomposition into CO_2 , CO and Y_2O_3 was complete at 640°.

In the DTA curve (Fig. 2), all the phases in the decomposition of $Y_2(C_2O_4)_3 \cdot 9 H_2O$

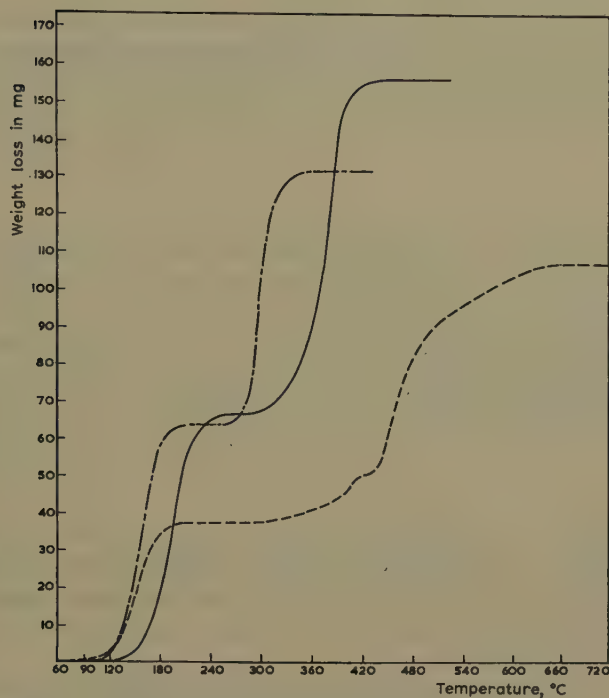


Fig. 1. Thermal decomposition of yttrium oxalate, cerous oxalate and zirconyl oxalate.
 — — — yttrium oxalate; — · — · — · cerous oxalate; ——— zirconyl oxalate.

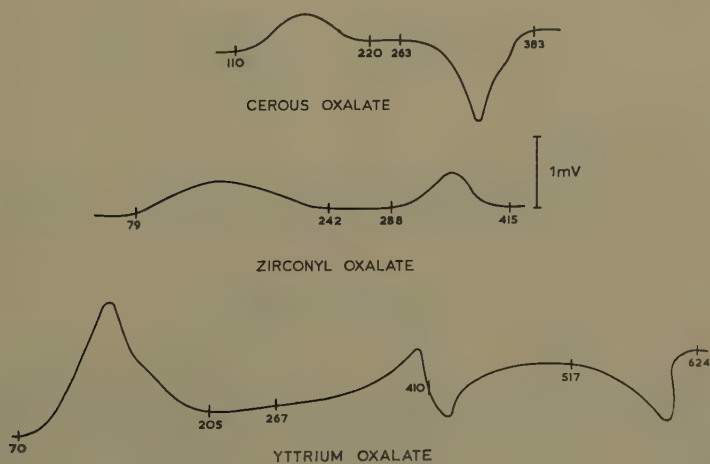


Fig. 2.

to 410°, were similar to those in the thermogram but between 410° and 468°, a new phase appeared which was neither shown up in the above thermogram nor in that of WENDLANDT. This phase further decomposed giving Y_2O_3 at 624°.

A new sample of $Y_2(C_2O_4)_3 \cdot 9 H_2O$ was very gradually heated in the DTA furnace

until a temperature of about $468 \pm 5^\circ$ was reached. The furnace was then maintained at this temperature for about 30 min and the sample removed and air quenched. A portion of the product was then analysed. No oxalate was present. The estimation of CO_2 and Y_2O_3 in the sample showed that the formula of this intermediate product was $(\text{YO})_2\text{CO}_3$.

Cerous oxalate

The compound prepared for this study corresponded to $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$. The thermogram (Fig. 1) showed that it began to yield its water of hydration at 90° , and the anhydrous $\text{Ce}_2(\text{C}_2\text{O}_4)_3$ was obtained at 220° . The decomposition of the anhydrous compound commenced at 268° and was completed at 365° . The final end product analysis was found to be CeO_2 .

The data obtained here fully agree with that of WENDLANDT³. DTA studies also gave results (Fig. 2) identical to those obtained above from thermogravimetric analysis.

Zirconyl oxalate

The thermogram (Fig. 1) showed that the decomposition of $\text{ZrO}(\text{C}_2\text{O}_4) \cdot 3\text{H}_2\text{O}$ started at 85° and the dehydration was complete at 256° . The anhydrous oxalate decomposed rapidly from 285° and finally resulted in ZrO_2 . Similar results were also obtained by DTA (Fig. 2).

CALCULATIONS OF RATE PARAMETER

To evaluate the kinetics of decomposition of the three oxalates by the thermogravimetric method, the following equation was used¹:

$$\frac{-\frac{E^*}{2.3R} \Delta(T^{-1})}{\Delta \log W_r} = -x + \frac{\Delta \log (dw/dt)}{\Delta \log W_r}$$

where E^* = energy of activation,
 x = order of reaction,
 T = absolute temperature,
 t = time,
 W_r = weight loss at completion of reaction minus weight loss up to time t ,
 dw/dt = rate of loss of weight with time,
 R = gas constant.

$$\frac{\Delta \log (dw/dt)}{\Delta \log W_r} \text{ vs. } \frac{\Delta(T^{-1})}{\Delta \log W_r}$$

was plotted for all the three metal oxalates. The order of reaction and the activation energy of dehydration and decomposition of the oxalates were calculated from the above curves.

The relation derived for the shape of DTA curves and the kinetics of the reaction in liquid by BORCHARDT and DANIEL² has been found to apply to the studies of solids. The relation for the first order reaction is given by

$$k = \frac{C_p \left(\frac{dT}{dt} \right) + K \Delta T}{K(A - a) - C_p \Delta T}$$

where k = rate constant of reaction,
 A = total DTA curve area,
 C_p = total heat capacity of reactant solid or reference solid,
 K = cell constant,
 $d\Delta T/dt$ = shape of curve at time t ,
 ΔT = height at time t ,
 a = area at time t .

quantities $C_p \frac{d\Delta T}{dt}$ and $C_p \Delta T$ are small, equation (2) could be reduced to

$$k = \frac{\Delta T}{A - a} \quad (2a)$$

The equation was extended to solids as the heat capacities of the reference material and the sample under study would not differ extensively if the packing of both cells were done the same way. From the plot of $\ln k$ vs. $1/T$, the activation energy E could be calculated from the equation

$$k = A'e^{-E/RT}$$

Typical plots for these equations are represented in Figs. 3 and 4, and the results summarized in Table I. It will be observed that there is good agreement between the values of decomposition temperatures obtained by DTA and thermogravimetry. Also there is fairly good agreement found between the values of the activation energy

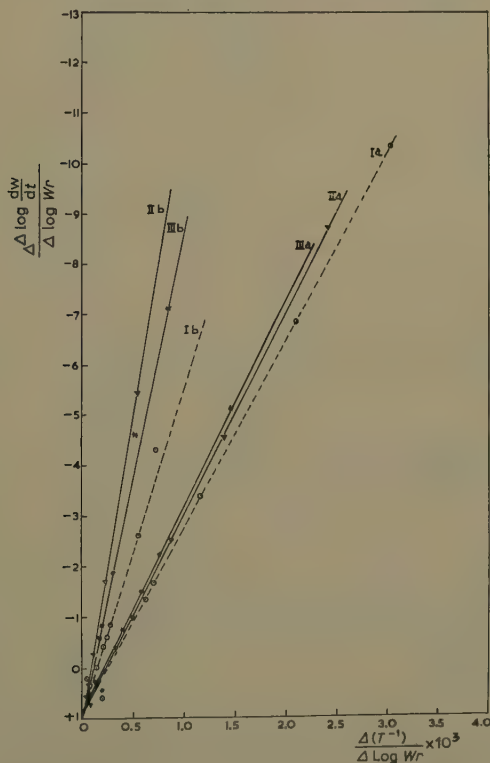


Fig. 3. Activation energy and order of reaction thermogravimetric method. — ○ — yttrium oxalate; — Δ — cerous oxalate; — * — zirconyl oxalate.

obtained from these two data, the assumptions made by PADMANABHAN *et al.*⁵ appear to be corroborated.

In the case of cerous oxalate, separate experiments were done to study its mod

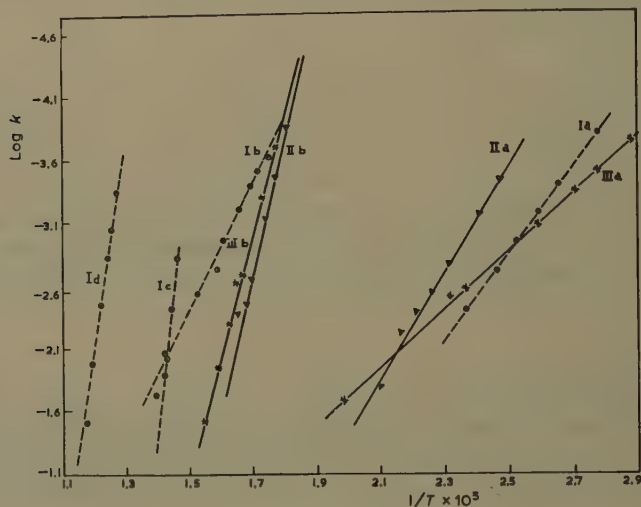


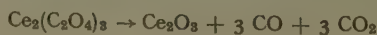
Fig. 4. Activation energy curve (DTA) —○— yttrium oxalate; —△— cerous oxalate; —*— zirconyl oxalate.

TABLE I
DECOMPOSITION OF Y, Ce(III) AND ZrO OXALATES

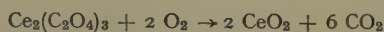
	Temperature of decomposition		Energy of activation		Order of reaction
	TGA	DTA	TGA in kcal/mol	DTA	
1. Yttrium oxalate					
$Y_2(C_2O_4)_3 \cdot 9 H_2O \rightarrow Y_2(C_2O_4)_3 \cdot 2 H_2O + 7 H_2O$					
$Y_2(C_2O_4)_3 \cdot 2 H_2O \rightarrow Y_2(C_2O_4)_3 + 2 H_2O$	60°	70°	17	17	0.5
$Y_2(C_2O_4)_3 \rightarrow (YO)_2CO_3 + 2 CO_2 + 3 CO$	260°	267°	30	24	0.5
$(YO)_2CO_3 \rightarrow Y_2O_3 + CO_2$	415° ^a	410°	—	105	
	—	517°	—	78	
2. Cerous oxalate					
$Ce_2(C_2O_4)_3 \cdot 10 H_2O \rightarrow Ce_2(C_2O_4)_3 + 10 H_2O$	90°	110°	18.5	20	0.5
$Ce_2(C_2O_4)_3 \rightarrow Ce_2O_3 + 3 CO + 3 CO_2$					
$Ce_2O_3 + O \rightarrow 2 CeO_2$	268°	263°	56	51.5	1.5
$3 CO + 3 O \rightarrow 3 CO_2$					
3. Zirconyl oxalate					
$ZrO(C_2O_4) \cdot 3 H_2O \rightarrow ZrO(C_2O_4) + 3 H_2O$	85°	79°	18	11	0.5
$ZrO(C_2O_4) \rightarrow ZrO_2 + CO_2 + CO$	285°	288°	44	44.5	1.5

^a Only a single step was observed.

decomposition. A weighed amount of the cerous oxalate was heated in the absence of air and the gases produced were analysed. The decomposition corresponds to



the presence of air or oxygen, analysis of the gases showed that the decomposition corresponds to



the DTA and the TGA were both done in air, the activation energies given in column 4 of Table I are for the overall reactions as shown in the first column.

ACKNOWLEDGEMENT

The authors wish to thank Dr. J. SHANKAR for helpful suggestions.

SUMMARY

The kinetics of the decomposition of yttrium, cerous and zirconyl oxalates have been studied thermogravimetrically and also by differential thermal analysis.

RÉSUMÉ

Les auteurs ont effectué une étude sur la décomposition des oxalates d'yttrium, de cérium(III)-zirconyle, par thermogravimétrie et par analyse thermique différentielle.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Kinetik der Zersetzung von Yttrium-, Cerium(III)-Zirkonyloxalat mit Hilfe der Thermogravimetrie und durch differentialthermische Analyse.

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ANION EXCHANGE STUDIES OF ZIRCONIUM(IV) IN CITRATE SOLUTION

SEPARATION FROM MIXTURES

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Ion exchange studies of the important fission product elements¹ have been continuing. Zirconium(IV) has been investigated. Zirconium(IV) is known to form a strong anionic citrate complex in 5% citric acid solution at pH *ca.* 2.7. TOMPKINS, KHOPKAR *et al.*² used this for the elution of zirconium in presence of fission products such as cerium, barium and strontium. The cation exchange separation³ of zirconium from titanium involved essentially the same principle; zirconium was completely eluted with 1% citric acid at pH *ca.* 1.75. The probable nature of the anionic citrate complex was found to be $[\text{ZrO}(\text{HCit})_2]^{-2}$ at low pH, whereas $(\text{ZrOCit})^{-}$ was predominant at higher pH.

KORKISCH AND FARAG⁴ developed the anion exchange separation of zirconium from thorium, titanium, iron and aluminium by using the anionic sulphate complex of zirconium in 0.1 *N* sulphuric acid. Zirconium was then eluted with 4 *N* hydrochloric acid. This method was extended⁴ for the determination of zirconium in silicate rocks. These workers have also studied the behaviour of the anionic ascorbate complex of zirconium on an anion exchanger. The fluoride or oxalate complexes of zirconium were used for its separation from hafnium on Dowex-1 resin, with 0.5 *N* hydrofluoric acid and 1 *N* hydrochloric acid as eluant. HUFFMANN *et al.*⁶ used a similar principle for their separation with 0.2 *N* hydrochloric acid and 0.01 *N* hydrofluoric acid. The anionic chloride complex⁷ of zirconium in 9 *N* hydrochloric acid formed the basis of the separation of zirconium from hafnium, niobium and tantalum. Zirconium has been separated from protoactinium⁸ on Amberlite IRA-400 with 6–7 *N* hydrochloric acid as an eluant, and from aluminium⁹ on Dowex-1 by means of its anionic complex in 0.06 *N* hydrochloric acid plus 0.8 *N* hydrofluoric acid.

However, no ion exchange studies of zirconium in citrate systems have been done so far. This paper describes such studies. The strongly basic quaternary ammonium type of anion exchanger Dowex 21K was utilised. Nitric acid, hydrochloric acid, perchloric acid and ammonium chloride were studied as the eluants. Zirconium was also separated from the important fission product elements *e.g.*, barium, strontium, caesium, cadmium, antimony, and also from lead and molybdate.

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APPARATUS AND REAGENTS

Apparatus

Ion-exchange column and Cambridge pH meter. The ion exchange column was identical to that previously described¹; a resin bed 1.4×14.5 cm was utilised.

Reagents

Zirconium oxychloride stock solution, 5.24 mg per ml; 5.529 g of zirconium oxychloride (E. Merck & Co.) was dissolved in 300 ml of water containing about 2% hydrochloric acid. The solution was standardised gravimetrically as the oxide¹⁰. For an exchange runs 36.68 mg of zirconium was taken.

Dowex 21K, (Dow Chemical Company, Midland, Mich. U.S.A.) 50–100 mesh, chloride-form anion exchange resin. This resin was conditioned as described earlier¹. The resin was converted to the citrate form by washing with 50 ml of 5% citric acid solution and then with water till the effluent was free from citric acid. At the conclusion of the runs, the resin was withdrawn from the column, air-dried, dried in an oven at 100° for 1–2 h and weighed.

Chemicals used were all of reagent grade, unless otherwise mentioned.

EXPERIMENTAL, RESULTS AND DISCUSSION

Anion exchange behaviour studies

An aliquot of zirconium oxychloride solution containing 36.68 mg of zirconium was mixed with 25 ml of water in a 50-ml beaker. Solid citric acid was added to this, so that the solution was 5% with respect to citric acid and the pH was adjusted to 2.7–2.8 by means of 0.01 *N* ammonium hydroxide and 0.26 *M* citric acid solution with pH meter. The solution containing the anionic citrate complex of zirconium was passed through the resin column at a rate of 1 ml per min. After adsorption the column was washed with 100 ml of water, and zirconium was then eluted with 300 ml of the various eluants at a rate of 2 ml per min. The eluting agents used were nitric acid (0.25, 0.50, 1.0 and 2.0 *N*); hydrochloric acid (0.50, 1.0, 2.0 and 4.0 *N*); perchloric acid (0.25 and 1.5 *N*) and ammonium chloride (1 *M*). The effluent batch (300 ml) was analysed for zirconium as the oxide after the destruction of citric acid by the usual nitric–perchloric acid treatment. Since citric acid complicates the analysis, the citrate complex must be decomposed and the liberated citric acid must be completely removed before the determination of zirconium. However, citric acid can be completely destroyed by two or three evaporations with nitric and perchloric acids.

The results (Table I) show that with 300 ml of nitric acid (0.25–2.0 *N*), or hydrochloric acid (0.50–2.0 *N*) as the eluting agent, essentially quantitative recovery of zirconium was possible. With perchloric acid or ammonium chloride as eluant, elution was incomplete. Hydrochloric acid (0.50–2.0 *N*) is suitable for routine work because of its volatility in the analysis step. Higher concentrations of hydrochloric acid⁷ and phosphoric acid⁴ itself were not used owing to their tendency to form the anionic complexes.

Anion exchange separations

Barium, strontium, lead, cadmium and caesium do not form anionic citrate complexes at pH 2.7–3.0, and can therefore be easily separated from zirconium by the

TABLE I

BEHAVIOUR OF THE ANIONIC CITRATE COMPLEX OF ZIRCONIUM(IV) TOWARDS VARIOUS ELUANTS

Zirconium = 36.68 mg; wt. of resin = 8.1476 g (oven dried)

No.	Eluting agent	Eluant concentration M	Total zirconium recovery %
1	HNO ₃	0.25	96.3
	HNO ₃	0.50	100.7
	HNO ₃	1.0	97.3
	HNO ₃	2.0	102.3
2	HCl	0.50	97.1
	HCl	1.0	102.1
	HCl	2.0	97.7
	HCl	4.0	104.7
3	HClO ₄	0.25	7.3
	HClO ₄	1.50	26.2
4	NH ₄ Cl	1.0	2.0

TABLE II

ION EXCHANGE SEPARATIONS

Zr = 36.68 mg

No.	Foreign ion		Zirconium recovery %
	added	mg	
1	Ba	72.8	100.9
2	Ba	36.4	100.1
3	Sr	72.0	102.5
4	Sr	36.0	101.5
5	Pb	71.4	101.4
6	Pb	35.7	99.8
7	Cs	71.7	101.7
8	Cs	35.9	102.0
9	Cd	72.0	102.9
10	Cd	36.0	103.2
11	Sb	9.0	113.4
12	U(VI)	71.4	135.1
13	Th(IV)	18.7	145.3
14	Mo ₇ O ₂₄ ⁻⁶	35.6	104.9

above method. The zirconium complex is retained in the bed while the cations pass through the column; the column is then washed with 100 ml of water, and zirconium is eluted with 300 ml of 2 N hydrochloric acid and determined as before.

Quantitative separations were obtained (Table II) except when antimony, thorium and uranium were present. The high results obtained in these cases were due to the elements being adsorbed under the same conditions as zirconium. It was observed that monovalent and divalent metals generally formed complexes at pH greater than 3.0 and did not interfere in the separation, whereas the trivalent and tetravalent elements formed complexes below pH 3.0 and so interfered. The method can be extended

er a large number of cations and can be used for the purification of zirconium from commonly associated cations.

Among anions, the separation of molybdate and vanadate from zirconium was examined. These ions were adsorbed along with zirconium. Zirconium was stripped with 300 ml of 1 *N* hydrochloric acid, the bed was then thoroughly washed acid-free with distilled water and finally molybdate and vanadate were eluted with 200 ml of 1% sodium carbonate. Molybdate did not interfere, but vanadate gave high results. The separations of zirconium from barium, strontium, caesium, cadmium and molybdenum are significant since these metals are commonly associated as major fission product elements. Essentially similar separations can be achieved by using ethylenediaminetetraacetic acid (EDTA), but as EDTA causes complications in the effluent analysis, such studies were not undertaken.

The method can be adapted for large scale separations by using larger ion exchange columns. The total operations described in this work require 8–9 h. The results are reproducible to within $\pm 4\%$.

ACKNOWLEDGEMENT

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SUMMARY

The anion exchange behaviour of zirconium(IV) in a citrate system is described. Nitric acid, hydrochloric acid, perchloric acid and ammonium chloride were tested as eluants on Dowex 21K ion exchange resin. Zirconium is separated from fission product elements *e.g.*, barium, strontium, cadmium, caesium, molybdate and also from lead.

RÉSUMÉ

Les auteurs ont effectué une étude sur le comportement du zirconium, en vue de sa séparation des autres éléments d'anions d'avec les éléments de produit de fission, tels que Ba, Sr, Cd, Cs, Mo et Pb.

ZUSAMMENFASSUNG

Es wird gezeigt, dass Zirkonium von anderen Spaltprodukten wie Ba, Sr, Cd, Cs, Mo und Pb mit Hilfe von Ionenaustauschern getrennt werden kann.

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ION EXCHANGE RESINS IN STEEL ANALYSIS

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Ion exchange resins have been extensively used both in the analysis and study of many of the elements found in steels¹. For example YOSHINO AND KOJIMA² separated iron and titanium on a cation exchanger; KAKIHANA³ studied the behaviour of vanadium(V) on a polyfunctional sulphonated cation exchanger; FILIPPOVA⁴ separated molybdenum and tungsten by adsorption on a cation exchanger, and selective elution with alkali; SUSSMAN⁵ studied the behaviour of chromate solutions on anion exchangers; ALIMARIN AND MEDVEDEVA⁶ separated the molybdenum, vanadium, and tungsten present in steel by using a cation exchanger and a sulphuric acid-hydrogen peroxide solution of the steel; and HAGUE⁷ with an anion exchanger separated nickel, manganese, cobalt and iron by utilizing their ability to form chloro complexes.

However no systematic method has been described for the separation of chromium, vanadium and molybdenum from alloy steels by anion exchange resins and this paper describes such a separation of these metals before their quantitative estimation.

Iron is not normally estimated in steels, thus the ideal separation by ion exchange techniques would be the retention of all elements excepting iron. As the acidic character of an element increases with increasing valency it should be possible to separate vanadium(V), chromium(VI) and molybdenum(VI) from iron(III) and certain other elements by the use of an anion exchanger^{5,6,8}. The adsorption of vanadium(V), chromium(VI) and molybdenum(VI) above pH 2.2, the isoelectric point of vanadium, does occur on an anion exchanger as indicated in the following experimental details.

However at pH 2.2 iron can precipitate from solution, but this precipitation of ferric ions can be overcome by forming stable complexes of iron with oxygen donors such as oxalic acid, citric acid, acetic acid and polyhydric alcohols⁹, but with the exception of the monocarboxylic acid, acetic acid, increasing pH will aid the formation of anionic complexes. Thus at approximately pH 2.5 the iron(III)-mannitol complex is cationic yet sufficiently stable to prevent precipitation of the iron. The iron(III)-acetate complex, whilst not as stable as the mannitol complex, is also cationic. A mixture of acetic acid, mannitol and ammonium hydroxide can then be used to adjust pH to approximately 2.5-3 with the iron still in solution as a cationic complex.

Phosphoric acid must be absent as it causes precipitation of a complex ferric phosphate¹⁰ at about pH 2, and also keeps tungsten in solution. Tungsten (VI) is adsorbed by anion exchangers but its elution is unsatisfactory due to colloidal formation

d solution. The removal of tungsten is achieved by digesting the steel solution and filtering before adding to the resin column.

EXPERIMENTAL

study of the behaviour of the elements concerned on the strongly basic anion exchanger DE-ACIDITE FF was first carried out. The elements were adsorbed on individual columns, containing approximately 25 ml of resin in the chloride form, in faintly alkaline 0.1 *M* vanadate, chromate, and molybdate solutions. 250 ml of various eluting agents were passed down the column at controlled rates. Versenate the sodium salt of ethylenediammine tetraacetic acid and sodium hydroxide was used throughout for pH adjustment.

A summary is given in Tables I–III of the results obtained. The actual elution values are dependent on such factors as weight of resin, volume of eluting agent and flow rates. However in the quantitative sense values of 0% and 100% only are of value. The findings indicate that, relatively, vanadium(V) is only weakly adsorbed by the resin, that chromium(VI) is strongly adsorbed and in fact that reduction to chromium(III) is necessary for its elution, and that molybdenum(VI) is quite strongly adsorbed especially on forming complexes such as the chloro compound. This chloro complex formation of molybdenum is well illustrated in Table III.

TABLE I
ELUTION STUDIES ON VANADIUM(V)

<i>Eluting agent</i>	<i>Strength</i>	<i>% Elution</i>	<i>Remarks</i>
HCl	0–0.5 <i>N</i>	0–75	increasing elution with increasing acid strength
HCl	0.5–10 <i>N</i>	100	some reduction to vanadium(IV)
H ₂ SO ₄	0–0.5 <i>N</i>	0–90	increasing elution with increasing acid strength
H ₂ SO ₄	0.5–10 <i>N</i>	100	
H ₃ PO ₄	0–1 <i>N</i>	0–50	increasing elution with increasing acid strength
H ₃ PO ₄	2–8 <i>N</i>	50–100	elution slow
Oxalate	pH 2–11	0–100	elution slow
Versenate	pH 4–12	0–100	increasing elution with increasing pH value
Citrate	pH 2–12	0–100	increasing elution with increasing pH value
NaOH	0–0.5 <i>N</i>	0–100	quantitative elution at 0.5 <i>N</i>
NaOH	0.5–8 <i>N</i>	100	elution rapid beyond 2 <i>N</i>
NH ₄ OH	0.5–10 <i>N</i>	10–30	very slow qualitative elution

From the results given in Tables I–III, at least one separation technique has been shown possible, namely

- a) Elution of vanadium with 0.6 *N* sodium hydroxide.
- b) Elution of chromium with at least 4 *N* hydrochloric acid.
- c) Elution of molybdenum with 1 *N* hydrochloric acid.

TABLE II
ELUTION STUDIES ON CHROMIUM(VI)

<i>Eluting agent</i>	<i>Strength</i>	<i>% Elution</i>	<i>Remarks</i>
HCl	0.1 <i>N</i>	Nil	Chromium reduced to trivalent state elution rapid beyond 6 <i>N</i>
HCl	4-10 <i>N</i>	100	
H ₂ SO ₄	0.1 <i>N</i>	Nil	slow elution increasing with increasing acid strength Cr(III) formed
H ₂ SO ₄	2-10 <i>N</i>	0-80	
H ₃ PO ₄	0.1 <i>N</i>	Nil	very slight slow elution at 8 <i>N</i> acid strength
H ₃ PO ₄	2-8 <i>N</i>	0-10	
Oxalate	pH 2-12	trace	very slow qualitative elution at higher pH values
Versenate	pH 4-12	Nil	
Citrate	pH 2-12	0-10	very slow qualitative elution at higher pH values Cr(III) formed
NaOH	0-0.5 <i>N</i>	Nil	slow qualitative elution at higher strengths
NaOH	0.5-10 <i>N</i>	0-5	
NH ₄ OH	0.5-10 <i>N</i>	Nil	

TABLE III
ELUTION STUDIES ON MOLYBDENUM(VI)

<i>Eluting agent</i>	<i>Strength</i>	<i>% Elution</i>	<i>Remarks</i>
HCl	0.2 <i>N</i>	0-100	increasing elution with increasing acid strength
HCl	4-10 <i>N</i>	Nil	chloro complex strongly adsorbed
H ₂ SO ₄	0.2 <i>N</i>	0-10	very slow qualitative elution
H ₂ SO ₄	4-10 <i>N</i>	50-90	slow elution
H ₃ PO ₄	0.1 <i>N</i>	Nil	slow elution increasing with increasing pH values elution very slow
H ₃ PO ₄	2-8 <i>N</i>	0-20	
Oxalate	pH 2-12	0-50	
Versenate	pH 4-12	0-70	slow elution at higher pH values
Citrate	pH 2-12	0-50	slow elution increasing with increasing pH values
NaOH	0-0.8 <i>N</i>	Nil	increasing elution with increasing alkali concentration
NaOH	1-10 <i>N</i>	0-100	
NH ₄ OH	0.5-10 <i>N</i>	Nil	

Other separations may also be possible but this selected separation is rapid and does not involve the formation of very stable complexes which could interfere in subsequent estimations.

Method of separation

A 0.5000-g sample of the alloy steel was dissolved in 20 ml of 4 *N* sulphuric acid. A few drops of nitric acid were then added and the solution digested for at least one hour. After filtering off the insoluble matter and precipitated tungsten, 5 ml 1 *N* silver nitrate solution were added to the filtrate followed by a few drops of 5% permanganate solution and some 2 g of ammonium persulphate. After developing the permanganate colour by boiling, 15 ml 1 *N* sodium chloride were added and the boiling continued to destroy the permanganate colour. On cooling, the solution was filtered if necessary, 1 g mannitol and 2 g ammonium acetate added and the volume adjusted to approximately 200 ml. The pH was then adjusted by dropwise additions of concentrated ammonium hydroxide to a value of 2.5–3. (The deep brown colour that develops serves as a useful guide to the volume of alkali required).

The solution was next added to the basic anion exchanger, DE-ACIDITE FF, approximately 25 ml of the resin having been lightly packed into a burette and converted to the nitrate form with sodium nitrate. The flow rate during adsorption and the subsequent water wash was of the order of 15 drops per min, and the total volume of solution and wash liquid was approximately 300 ml. The washing technique, as in the adsorption step, was downflow by inserting a flask fitted with a glass tube, at an angle at the outlet end, into the top of the resin column.

Elution of the adsorbed vanadium, chromium and molybdenum was the next step. Some 200 ml 0.6 *N* sodium hydroxide was passed down the column at a flow rate of 5–10 drops per min followed by a water wash at the same flow-rate to give a final volume of 250 ml. This was then reserved for vanadium estimation. The chromium was eluted next with 200 ml 8 *N* hydrochloric acid at a flow rate of 5–10 drops per min and the washings made up to 250 ml with water. No water wash of the resin was used to avoid a premature elution of molybdenum. Finally the molybdenum was eluted with 200 ml 1 *N* hydrochloric acid at a flow rate of 5–10 drops per min, and the volume adjusted to 250 ml.

Estimation of the separated metals

Vanadium was estimated spectrophotometrically by the hydrogen peroxide method using 50-ml aliquots^{11,12}.

Chromium was estimated spectrophotometrically using the diphenylcarbazide method^{11,12}. The 5-ml aliquot of chromium solution was first oxidised to the hexavalent state with bromine in alkaline solution and the excess bromine removed with ascorbic acid.

Molybdenum was estimated on a 25-ml aliquot by the thiocyanate colorimetric method^{11,12}.

TABLE IV

<i>Element</i>	<i>No. 1</i>	<i>No. 2</i>	<i>No. 3</i>
Vanadium	0.82%	1.02%	0.30%
Chromium	3.32%	4.08%	2.50%
Molybdenum	0.55%	0.40%	0.50%
Tungsten	16.12%	18.05%	10.02%
Nickel	0.43%	0.09%	2.84%
Cobalt	4.35%	0.11%	Nil
Manganese	0.22%	0.33%	0.30%

RESULTS

The certified steels chosen for the analyses had a composition as mentioned in Table IV. The results of seven separate analyses on each steel are as given in Table V.

TABLE V

Element	Sample No.	Mean % found	Present %
Vanadium	1	0.79	0.82
Vanadium	2	0.97	1.02
Vanadium	3	0.29	0.30
Chromium	1	3.28	3.32
Chromium	2	4.00	4.08
Chromium	3	2.47	2.50
Molybdenum	1	0.52	0.55
Molybdenum	2	0.38	0.40
Molybdenum	3	0.48	0.50

Probable errors are: Vanadium $\pm 0.02\%$, Chromium $\pm 0.05\%$ and Molybdenum $\pm 0.02\%$.

These results compare favourably with those obtained using other separation techniques, such as the mercury cathode deposition, whilst the method can be readily adapted to the simultaneous analysis of many steel samples. The time for one or more analyses is approximately 6 h.

SUMMARY

The metals vanadium, chromium and molybdenum may be separated from the other constituents of steel by passing an acetate buffered solution of the steel through a strongly basic anion exchanger and selectively eluting the above metals from the resin column with aqueous solution of 0.6 N sodium hydroxide, 8 N hydrochloric acid and 1 N hydrochloric acid, respectively.

RÉSUMÉ

Une méthode est proposée pour la séparation du vanadium, du chrome et du molybdène d'autres métaux d'un acier, en utilisant des résines d'échange d'ions.

ZUSAMMENFASSUNG

Beschreibung eines Verfahrens zur Abtrennung von Vanadium, Chrom und Molybdän von anderen Metallen in Stahl mit Hilfe von Ionenaustauschern.

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USE OF CARBOXYLIC ACID CATION EXCHANGE RESIN IN THE ANALYSIS OF COPPER IN CHROMATED WOOD PRESERVATIVE SOLUTIONS

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INTRODUCTION

Mixtures of copper sulphate-sodium dichromate, copper sulphate-zinc sulphate-sodium dichromate, copper sulphate-sodium arsenate-sodium dichromate and copper sulphate-borax-sodium dichromate are widely used as wood preservatives. The method usually employed for the analysis of copper in these solutions involves the removal of dichromate by a series of rather lengthy analytical operations¹. The successful application of cation exchange resins (sulphonic acid resins) to isolating copper from water^{2,3} and milk⁴ prior to its estimation, indicated that an improved method for separating copper from dichromate could be developed by a similar approach. This paper describes the use of carboxylic acid resins for this purpose. Because of the high selectivity of these resins for copper⁵, together with their ease of regeneration⁶, only small sized resin columns are required. This will reduce the time required for the separation. Carboxylic acid resins, unlike sulphonic acid resins, have received little attention in analytical chemistry.

EXPERIMENTAL

Retreatment of ion exchange resin

Fines were removed from 20-30 g Amberlite IRC-50 0.3-0.5 mm resin by repeatedly washing the resin with water, allowing the larger particles to settle and decanting off the fines. The resin was slurried into a 20 cm long, 2 cm internal diameter ion exchange column of conventional design.

Absorbed metals were removed from the resin by washing it with 200 ml 2 N HCl.

The resin was washed with 250 ml deionised water before being converted into the ammonium form by treatment with 200 ml 2 N NH₄OH and 200 ml 2 N NH₄Cl at a flow rate of 0.25 ml/min.

The resin was finally washed with 200 ml deionised water, removed from the column, air dried and stored in a polythene bottle.

Preparation of ion exchange column

A 5-cm long resin bed was prepared in a 22-cm long pyrex tube having an inside diameter of 1 cm and fitted with a ground-glass tap at the lower end. The resin bed was supported on a glass wool plug. Under the working conditions employed below, a column of the above dimensions had a break-through capacity of 1.4 mequiv. Cu²⁺.

PROCEDURE

An aliquot of wood preservative solution containing 0.2–0.6 mequiv. Cu^{+2} was pipetted into a small beaker and 5 *N* NH_4OH was added dropwise until the precipitate of basic copper salt had dissolved. An additional 2–3 drops of NH_4OH solution were then added. The resultant solution was transferred to the column head and soaked into the resin at a flow rate of 0.25 ml/min. 10 ml deionised water was used to complete the transfer of the sample to the column. A blue band of absorbed copper ions was clearly visible at the top of the resin bed at this stage. When the liquid level in the column head had almost reached the top of the resin bed, the resin was washed with 20 ml deionised water at a flow rate of 0.25 ml/min. The effluent, which contained the anions present in the preservative solution, was discarded. When the liquid level in the column had almost reached the top of the resin bed, the absorbed copper was eluted with 20 ml 2 *N* HCl at a flow rate of 0.25 ml/min. The HCl effluent was collected in a 150-ml beaker. After adjusting the pH of the hydrochloric acid effluent to 4.0–4.5 with ammonium hydroxide and acetic acid, the copper was estimated volumetrically with standard thiosulphate solution. On completion of the elution stage the resin was transferred to a used resin container. When sufficient resin had accumulated, it was treated from \square under *Pretreatment of ion exchange resin*.

RESULTS

Known amounts of a synthetic copper sulphate–sodium dichromate solution (0.47 $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ and 0.75 g $\text{Na}_2\text{Cr}_2\text{O}_7/100 \text{ ml}$) were analysed by the procedure described above. The results are listed in Table I.

A number of commercial chromated wood preservative solutions were also analysed. The results are given in Table II.

TABLE I

<i>Cu present (mg)</i>	<i>Cu found (mg)</i>	<i>Recovery (%)</i>
6.0	6.0	100.0 (99.2)
	5.9	98.3
12.0	12.0	100.0 (100.0)
	12.0	100.0
24.0	23.9	99.5 (99.8)
	24.0	100.0

TABLE II

<i>Preservative</i>	<i>Cu present in 10 ml aliquot (mg)^a</i>	<i>Cu found by present procedure (mg)</i>	<i>Recovery (%)</i>
Chromated copper sulphate	5.1	5.1	100.0 (100.0)
		5.1	100.0
Chromated copper arsenate	10.0	10.1	101.0 (100.0)
		9.9	99.0
Chromated copper sulphate–Borax	15.3	15.2	99.3 (99.7)
		15.3	100.0

^a Determined gravimetrically with cupron⁷.

DISCUSSION

The cation exchanger was converted to the ammonium form before use for the following reasons. Exchange rates are higher when the resin is in the salt form⁶. If the resin is in the hydrogen form, the hydrogen ions liberated by the uptake of the Cu^{+2} ions may upset the pH of the influent solution and cause incomplete uptake of the Cu^{+2} ions. Cations are not taken up appreciably by carboxylic acid resins⁶ in solutions of low pH 7.

The time taken for the proposed method was approximately half-an-hour. Because of its simplicity, the present method lends itself to multiple routine analysis. For this purpose a number of columns can be arranged in series so that one column is available for each sample.

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SUMMARY

A cation exchange separation, using carboxylic acid resin, combined with a thiosulphate titration suggested as a rapid and accurate method for the determination of copper in chromated wood preservatives.

RÉSUMÉ

Une méthode est proposée pour le dosage du cuivre dans des solutions destinées au traitement du bois (séparation par une résine d'échange d'ions et titrage par le thiosulfate).

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Kupfer in Holzimprägnierungsmittel durch Titration mit Thiosulfat nach vorheriger Trennung von Chromat mit Hilfe eines Ionenaustauschers.

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THE APPLICATION OF CHELATE SYSTEMS TO PARTITION
CHROMATOGRAPHY: PRELIMINARY PAPER

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INTRODUCTION

A considerable amount of effort has been devoted in the past to the development of techniques which may be used for the separation of metals, and of these, two methods, solvent extraction and chromatography, have been very widely applied.

In both cases, the distribution of a metal, in one or more forms, between two phases is involved, but whereas solvent extraction most frequently utilizes an immiscible liquid-liquid solvent pair, in chromatography other than gas chromatography the phases are either a liquid and a solid, or else two liquids, one of which is rendered immobile by retention on a solid. The selectivity of this type of process can usually be considerably improved by careful control of acidity, and the addition of competitive complexing agents to one or both phases.

Solvent extraction has gained much favour by virtue of the very wide range of organic and inorganic ligands available that can be used in combination to afford the satisfactory separation of many metals. However, if the separation factor for two metals is not large even under optimum conditions, it will be necessary to repeat the extraction a number of times. If a batch extraction technique is used it is likely to prove both time consuming and tedious.

In order to overcome this difficulty, continuous¹ and continuous countercurrent methods have been devised in which one or both of the phases involved in the extraction process are continuously replaced, whilst discontinuous countercurrent equipment³ will allow a large number of batch extractions to be carried out in sequence with comparative ease.

The nature of the species involved in the distribution of a metal between a chromatographic column and a solvent cannot be as widely varied as between two solvents, but since a solute passing through a column undergoes a series of successive equilibrations, even small separation factors are of value. It would clearly be an advantage if the complexing agents, familiar in liquid-liquid extractions could be used in the form of a column, and this has been done already for 8-hydroxyquinoline⁴, 8-hydroxyquinoline, β -naphthoquinoline and cupferron, either alone or mixed with potassium starch⁵ and dimethyl glyoxime, either alone or mixed with calcium carbonate or magnesium carbonate⁶.

Direct interaction of this kind between a metal in aqueous solution and the solvent complexing agent is likely to occur extremely slowly if one of the very hydrophobic

ands is used, and a wetting agent must be added to the aqueous phase to achieve reasonable reaction rate. This complication has been avoided by CARRITT⁷ who made columns of cellulose acetate coated with dithizone which he "wetted" with a small amount of carbon tetrachloride before passing the aqueous solution through them. These columns have proved rather unstable, but there would appear to be advantages in a reverse phase partition technique of this type in which the organic phase is held stationary since it requires the minimum pretreatment of the metal solution. For satisfactory operation the solvent must adhere firmly to the support material, so both the complexing agent and the metal complex should have large partition coefficients in favour of the organic phase, if they are not to be eluted off the column in appreciable quantities.

It has been found that these requirements are fulfilled by solutions of certain complexing agents on silica gel and in this paper preliminary work is reported which has been carried out to determine the behaviour of dithizone in such a system. Since the inception of this work a reverse phase partition method for the separation of cerium has been reported⁸.

THEORETICAL CONSIDERATIONS

The reaction between an n -valent metal M^{+n} and dithizone, here represented as a monobasic acid HL, in the aqueous phase of a two phase system is conventionally represented by



with an equilibrium constant for the reaction K where

$$K = \frac{[ML_n][H^+]^n}{[M^{+n}][HL]^n} \quad (1)$$

square brackets denoting concentrations, which are used in place of activities for solutions of constant ionic strength. The chelate and reagent are assumed to partition to an organic phase with partition coefficients P_c and P_r such that

$$P_c = \frac{[ML_n]_0}{[ML_n]} \quad (2a)$$

$$P_r = \frac{[HL]_0}{[HL]} \quad (2b)$$

the subscript 'o' distinguishing the species in the non-aqueous phase. Provided that the equilibria in the system are accounted for by equations (1), (2a), (2b), it has been shown by numerous authors⁹ that

$$\frac{[ML_n]_0}{[M^{+n}]} = \frac{KP_c}{P_r^n} \cdot \frac{[HL]^n_0}{[H^+]^n} = \frac{K'[HL]^n_0}{[H^+]^n} \quad (3)$$

the fraction extracted is defined by

$$E = \frac{\Sigma[M]_0}{\Sigma[M]}$$

in the simplest case, where P_c is large and it is possible to neglect lower dithizone

complexes, ML , $ML_2 \dots ML_{n-1}$, and other complexes MX , $MX_2 \dots MX_j$ (which may be cationic or anionic), $[ML_n]_0/[M^{+n}]$ may be identified with the fraction extracted. If an anion X^- is present in the aqueous phase, which is capable of forming the non-extractable species $MX^{+(n-1)} + \dots + MX_n$ with the metal M^{+n} , then

$$\begin{aligned}\Sigma[M]_w &= [M^{+n}] + [MX^{+(n-1)}] + \dots + [MX_n] \\ &\doteq [M^{+n}] \{1 + K_1[X^-] + K_1K_2[X^-]^2 + \dots + K_1K_2 \dots K_n[X^-]^n\}\end{aligned}$$

the formation constant K_j being defined by

$$K_j = \frac{[MX_j^{+(n-j)}]}{[MX_{j-1}^{+(n-j+1)}][X^-]}$$

So equation (3) now becomes

$$E = \frac{K' [HL]_0^n}{[H^+]^n \{1 + K_1[X^-] + K_1K_2[X^-]^2 + \dots + K_1K_2 \dots K_n[X^-]^n\}}$$

It is frequently the practice in extraction experiments to maintain $[X^-]$ constant when equation (5) may be rewritten in a form similar to that of equation (3)

$$E = K'' \frac{[HL]_0^n}{[H^+]^n} \quad (3)$$

but now the constant refers to a particular X^- concentration in the aqueous phase.

Equation (5) could still account for the behaviour of a solution of chelating agent held on silica gel, during the extraction of a metal, if the only function of the support was to act as inert diluent. This would also be true if the non-aqueous solution were retained on the surface of the silica, but in the latter case the concentration per unit weight would vary with particle size.

Alternatively the behaviour of the dithizone-containing support may be considered to be closely analogous to that of an ion exchange resin in that it consists of an immobilised organic substrate, capable of exchanging its protons for metal ions present in the aqueous phase.

The immediate objects of the present work were to investigate the distribution of a metal between an aqueous phase and a solution of a chelating agent retained on silica gel, and by means of equation (5) to ascertain if the extraction process was similar to that involved in the corresponding liquid-liquid extraction.

EXPERIMENTAL

Silica gel was precipitated from sodium silicate solution with 10 *N* hydrochloric acid in the manner suggested for partition chromatography¹⁰, dried and graded, the fraction 85-120 mesh being retained.

Purification of the gel for use in the copper-dithizone system was carried out by allowing it to stand under successive volumes of concentrated hydrochloric acid until the supernatant acid remained colourless¹¹, then, after washing with water, it was shaken with a strong ethylenediamine-tetraacetic acid solution at a pH of approx-

ely 5. Finally, after again being washed with water, alcohol and ether, the gel was dried at 110° .

Silica gel, prepared in this way, was placed in a beaker and just covered with a 1% aqueous solution of dithizone, which had previously been purified¹². The organic solvent was then evaporated off until a freely running powder was obtained, which was stored in a desiccator over the organic solvent, in the dark. The dithizone content of the samples of treated silica gel, used in these experiments, was found to lie between 10^{-6} and 10^{-5} mol of dithizone per g of support, but this could be considerably increased if required.

Before being used the silica gel was removed from this desiccator, and exposed to air for 40 min to allow time for surplus organic solvent to evaporate and the gel to achieve constant weight.

20 ml of an aqueous hydrochloric acid phase and a weighed amount of silica gel (0.1 g) containing dithizone were placed in a 50-ml flask and a small amount (10^{-8} mol) of radioactive copper (^{64}Cu) added in hydrochloric acid solution. In liquid-liquid extractions the solid phase was replaced by 20 ml of a solution of dithizone in either chloroform or carbon tetrachloride.

The flask and its contents were then very gently shaken mechanically for half an hour on a wrist action shaker, a time longer than that found necessary for the system to come to equilibrium.

Only when both the acidity of the aqueous phase was high and the organic solvent was carbon tetrachloride, did the dithizone solution show any tendency to strip off copper from the support.

Solid-liquid extractions were duplicated with samples of silica gel treated with organic solvent, but no dithizone, and these experiments showed that in the absence of a chelating agent, no extraction occurred. It would therefore appear that removal of copper from the aqueous phase was effected by chelation only, and not by adsorption. Liquid phases were always presaturated with the other solvent present in the system.

After equilibration the contents of the flask were either filtered through a glass filter, which did not adsorb any copper at the acidities used, or centrifuged, and the activity and acidity of the aqueous phase determined. The activity was compared with that of a standard made up of 20 ml of the hydrochloric acid solution, and an amount of radioactive copper equal to that used in the extraction. Correction was made for the decay of 12.8 h copper.

The dithizone content of the silica gel was obtained as follows. A weighed amount of silica gel was treated with quantities of ammonia solution until all the dithizone was in aqueous solution. The combined aqueous extracts were made acid and the precipitated dithizone dissolved in a known volume of carbon tetrachloride. The optical density of this solution was measured, and using a value of $34.6 \cdot 10^3$ for the extinction coefficient of dithizone in carbon tetrachloride¹³ the dithizone content of the original sample calculated.

DISCUSSION

A plot of $\log E$ versus the acidity of the aqueous phase is given in Fig. 1 for the case where the organic solvent on the silica gel was carbon tetrachloride (line A), and is compared with a similar plot for the distribution of copper between an aqueous

hydrochloric acid phase and a dithizone-carbon tetrachloride phase (line B). Equivalent experiments with chloroform as the organic solvent gave the results plotted in Fig. 2.

If the species involved in the liquid-liquid and liquid-solid extractions are the same, then from equation (5)

$$\frac{E_A}{E_B} = \frac{K'_A ([HL]_0)_A^{n_A} [H^+]_B^{n_B} \{1 + K_1[X^-]_B + K_1K_2[X^-]_B^2 + \dots + K_1K_2 \dots K_n[X^-]_B^n\}}{K'_B ([HL]_0)_B^{n_B} [H^+]_A^{n_A} \{1 + K_1[X^-]_A + K_1K_2[X^-]_A^2 + \dots + K_1K_2 \dots K_n[X^-]_A^n\}}$$

where subscripts A and B refer to the liquid-solid and liquid-liquid systems respectively. If $[HL]_0$ is virtually unchanged by extraction, equation (6) reduces

$$\frac{E_A}{E_B} = K_{(HL)} \frac{[H^+]_B^{n_B} \{1 + K_1[X^-]_B + K_1K_2[X^-]_B^2 + \dots + K_1K_2 \dots K_n[X^-]_B^n\}}{[H^+]_A^{n_A} \{1 + K_1[X^-]_A + K_1K_2[X^-]_A^2 + \dots + K_1K_2 \dots K_n[X^-]_A^n\}}$$

and for the same hydrochloric acid concentration if $n_A = n_B$

$$\log E_A - \log E_B = \text{constant}$$

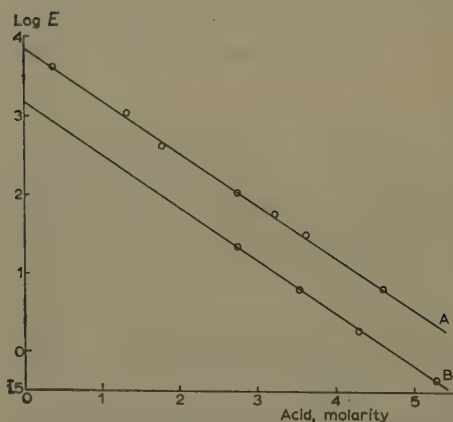


Fig. 1. The extraction of copper from an aqueous hydrochloric acid phase into a solution of dithizone in carbon tetrachloride. For curve A the solution was retained on silica gel. Dithizone concentrations, for curve A $2.4 \cdot 10^{-3}$ m/kg, for curve B $2.37 \cdot 10^{-4}$ m/l.

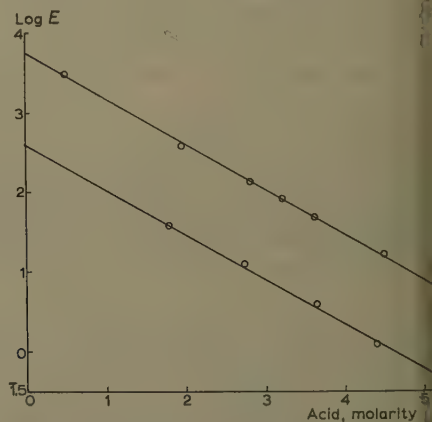


Fig. 2. The extraction of copper from an aqueous hydrochloric acid phase into a solution of dithizone in chloroform. For curve A the solution was retained on silica gel. Dithizone concentrations for curve A $7.9 \cdot 10^{-3}$ m/kg, curve B $6.0 \cdot 10^{-4}$ m/l.

Since curves A and B, Figs. 1 and 2, satisfy equation (8), and by comparison with the liquid-liquid system, it would appear that $n_A = n_B = 2$, implying that two protons are liberated during the formation of a complex between copper and dithizone retained on silica gel. The vertical separation of lines A and B will give a measure

$$\frac{K'_A ([HL]_0)_A^{n_A}}{K'_B ([HL]_0)_B^{n_B}}$$

and consequently if $([HL]_0)_A^{n_A}$ and $([HL]_0)_B^{n_B}$ are known K'_A/K'_B may be found. T

has not been calculated because of the lack of any accurate information as to the nature of the dithizone species on the silica gel.

The similarity in the extraction behaviour of the liquid-solid to the liquid-liquid system, suggests that the same control of the acidity of the aqueous phase, which is of such value for regulating the partition of the metal between the two phases of the solvent extraction system, may be equally well used to vary the fraction of metal extracted, when the chelating agent is retained on silica gel, and if this closeness in behaviour is maintained for the extraction of other metal dithizonates it should be possible to adapt many of the liquid-liquid separations to work on the column principle. Qualitative experiments, to be reported at a later date, have also shown that metals, held by a dithizone column of this type, may be eluted by aqueous solutions of complexing agents.

It would, therefore, seem that columns containing solutions of chelating agents have considerable potentialities for separating metals, since a normal chromatographic separation may be enhanced by the addition of sequestering reagents to the aqueous phase, and the careful control of acidity, to provide selective extraction or elution.

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SUMMARY

It has been found possible to retain solutions of chelating agents on a solid supporting medium, and in this paper preliminary investigations are reported which were carried out to determine the extraction behaviour of radioactive copper between an aqueous hydrochloric acid phase and a solution of dithizone in an organic solvent retained on silica gel. Chloroform was found to be a very satisfactory solvent and carbon tetrachloride was also used. For both of these solvents the extraction *vs.* acidity curves were found to be similar to the corresponding liquid-liquid extraction. The high values for the fraction extracted show that this method would provide a useful technique for the concentration of copper from aqueous solution, and the similarity between the liquid-liquid and liquid-solid extractions suggests that it may be possible to adapt conventional liquid-liquid extractions to work on the column principle.

RÉSUMÉ

Une étude préliminaire a été effectuée sur l'application des chélates à la chromatographie de partition. L'auteur a examiné le comportement d'un cuivre radioactif entre une phase aqueuse de chlorhydrique et une solution de dithizone dans un solvant organique, sur silicagel.

ZUSAMMENFASSUNG

Es wurde gefunden, dass chelatbildende Reagenzien von festem Trägermaterial, wie Silicagel, adsorbiert werden können. Es wurde das Verhalten von radioaktivem Kupfer in salzsaurer Lösung bei der Extraktion mit einem Dithizon enthaltenden organischen Lösungsmittel in Gegenwart von Silicagel untersucht. Auf die Möglichkeit der Anreicherung von Metallen durch Extraktion unter Zuhilfenahme von Kolonnen wird hingewiesen.

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COLORIMETRIC DETERMINATION OF URANIUM(VI)

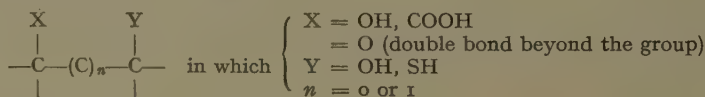
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Derivatives of salicylic acid have occasionally been used as reagents for the colorimetric determination of uranium(VI). Salicylic acid itself was employed by MÜLLER¹.

A study² of organic reagents for the identification and colorimetric determination of uranium(VI) has shown that this element reacts preferentially with organic reagents which contain the following general atomic grouping:



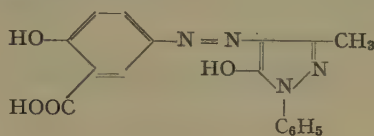
It was suggested that this group was the active functional group for uranium(VI). Three new reagents for uranium(VI) which possess this functional group were proposed, namely: the sodium salt of *p*-aminosalicylic acid, the sodium salt of *p*-nitrobenzene-azosalicylic acid (Alizarin Yellow R) and the sodium salt of *m*-nitrobenzene-azosalicylic acid (Alizarin Yellow G.G.). These reagents permit the colorimetric determination of uranium(VI) in the respective ranges 34.5–414 $\mu\text{g/ml}$, 6.9–69 $\mu\text{g/ml}$, and 6.9–82.8 $\mu\text{g/ml}$. Benzene-azosalicylic acid and Alizarin Yellow RS have also been proposed for the colorimetric determination of uranium², the respective ranges being 6.9–41.4 $\mu\text{g/ml}$ and 6.9–55.2 $\mu\text{g/ml}$.

Recently, the ammonium salt of 4,4'-bis-[(azo-5)-salicylic] acid was proposed for the colorimetric determination of uranium³.

In the present paper is described the colorimetric determination of uranium(VI) by means of a reagent which contains the above group and also an heterocyclic ring. This reagent was chosen because its diverse substituents favourably influence the se-

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activity of the reaction with uranium. The reagent is 1-phenyl-3-methyl-4-(3'-carboxy-hydroxyphenyl-azo)-pyrazol-5-one (I).



(I)

REAGENTS AND PROCEDURE

Reagent

A solution of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in water, containing $138 \mu\text{g U/ml}$. The reagent is used as a 0.2% solution in ethyl alcohol.

Experimental

To a 10-ml graduated flask were added a volume varying up to 3 ml of the uranium standard solution and 1 ml of the reagent solution, and the mixture was diluted to the mark with ethanol. A comparison solution was prepared containing the same quantity of reagent as the test solution. Readings were made with a M53 filter on a Belfrich vertical spectrophotometer (Russian model). Filters M43, M47 and M50 were not suitable for the extinction measurements. The pH of the solutions was always adjusted to a value of 5-6. The results of the determinations are shown in Tables I

TABLE I

$\mu\text{g U}/10 \text{ ml}$	496 $m\mu$	533 $m\mu$	574 $m\mu$	619 $m\mu$	665 $m\mu$
276	unreadable	0.65	0.12	0.04	0.00

TABLE II

ml of solution $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$	μg $\text{U(VI)}/10 \text{ ml}$	M53 Extinction
0.125	17.25	0.035
0.25	34.50	0.08
0.5	69	0.16
1.0	138	0.32
2.0	276	0.65
3.0	414	0.93

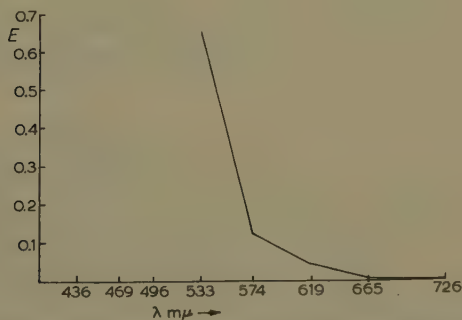


Fig. 1. The absorption spectra of the complex UO_2^{+2} -reagent I. $c = 276 \mu\text{g U(VI)}/10 \text{ ml}$.

and II; the absorption spectrum and extinction curves are recorded in Figs. 1 and 2.

The results given indicate that the proposed method is suitable for the colorimetric determination of uranium(VI) in the range 1.72–41.4 $\mu\text{g/ml}$; the method is therefore one of the most sensitive for this element.

The influence of pH on the extinction has been studied, the results being recorded in Fig. 3.

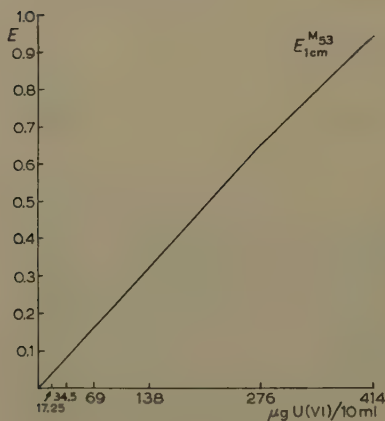


Fig. 2. The extinction curve of the complex UO_2^{+2} -reagent I.

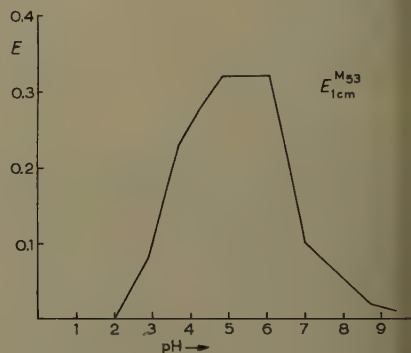


Fig. 3. The influence of pH on the extinction of the complex UO_2^{+2} -reagent I. $c = 1.72 \mu\text{g U(VI)/10 ml}$.

SUMMARY

A new, very sensitive reagent is proposed for the colorimetric determination of uranium(VI), namely 1-phenyl-3-methyl-4-(3'-carboxy-4'-hydroxyphenyl-azo)-pyrazol-5-one.

RÉSUMÉ

Le 1-phényl-3-méthyl-4-(3'-carboxy-4'-hydroxyphényl-azo)-pyrazol-5-one est proposé comme réactif pour le dosage colorimétrique de l'uranium(VI).

ZUSAMMENFASSUNG

Das 1-Phenyl-3-methyl-4-(3'-carboxy-4'-hydroxyphenyl-azo)-pyrazol-5-one wird als neues Reagenz für die colorimetrische Bestimmung von Uran vorgeschlagen.

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UTILISATION DE L'ACIDE PHÉNYLARSONIQUE
EN TURBIDIMÉTRIE

DOSAGE DU TANTALE

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INTRODUCTION

détermine habituellement de faibles quantités de tantale par une colorimétrie son composé avec le pyrogallol¹. Cette méthode, étant peu spécifique, nécessite séparations. La plus utilisée est, à l'heure actuelle, l'extraction du fluorure par xone en divers milieux¹⁻⁴. Mais cette séparation a pour but principal d'éliminer l'interférence du niobium; l'effet d'autres éléments a été peu étudié. On connaît par ailleurs, la spécificité de l'acide phénylarsonique en milieu acide⁵; MAJUMDAR⁶ a étudié la séparation gravimétrique de quantités pondérales de tantale et de niobium par précipité. Nous avons mis au point une méthode de dosage turbidimétrique par l'acide phénylarsonique, suffisamment sélective pour éliminer la plupart des séparations, et nous avons appliqué cette méthode au cas particulier d'un alliage uranium-tantale contenant de 0.5 à 2% de tantale.

ÉTUDE DE LA TURBIDIMÉTRIE

Matériaux

Acide phénylarsonique en solution aqueuse à 2%; glycérine en solution aqueuse à 20%.

Solutions étalons

Solution de sulfate d'uranyle à 100 g U/l; solution de niobium, 500 mg/l de niobium dans une solution à 5% d'acide tartrique; solution de tantale à 1 g/l obtenue par attaque nitrofluorhydrique du métal et élimination de l'acide fluorhydrique par évaporation en présence d'acide sulfurique; solution de zirconium à 100 mg/l obtenue par dissolution dans H₂SO₄ 2 N d'oxychlorure de zirconium „MERCK”.

Méthode opératoire

Dans une fiole de 10 ml, introduire environ 200 µg de Ta; acidifier par 1 ml d'acide sulfurique 12 N, ajouter 1 ml de la solution de stabilisant (glycérine), puis 1 ml d'acide phénylarsonique; compléter à 10 ml; bien agiter; déterminer la transmission au spectrophotomètre après 1/2 h d'attente.

Utilisation du précipité

La glycérine nous a donné les meilleurs résultats: l'absorption due au précipité est

constante pendant au moins une heure. Avec la gomme arabique les points s'alignent mal et la sensibilité est plus faible. La gélatine (1 ml à 10 %) empêche toute précipitation.

Courbes de transmission et choix de la longueur d'onde

En utilisant le mode opératoire décrit, on a déterminé les courbes de transmission de: 200 μg Ta, 50 μg Zr, 100 mg U, 100 mg U + 50 μg Zr.

Les résultats concernant les différentes solutions sont rassemblés dans le Tableau 1 et la Fig. 1. La cuve de référence contient de l'eau; la largeur de fente est égale 0,18 mm à 310 m μ avec une lampe à tungstène.

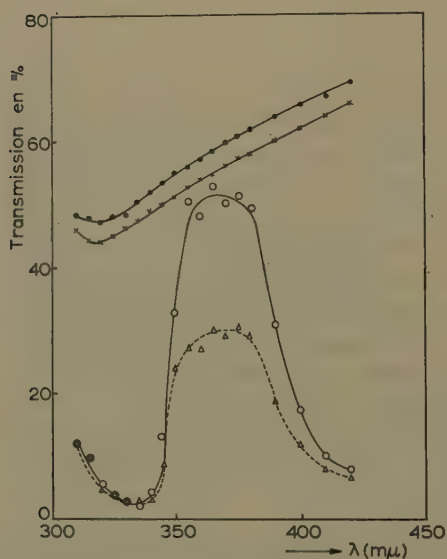


Fig. 1. Turbidimétrie du zirconium et du tantale à l'acide phénylarsonique. Courbes de transmission: ● = 50 μg Zr; × = 200 μg Ta; ○ = 100 mg U; Δ = 50 μg Zr + 100 mg U.

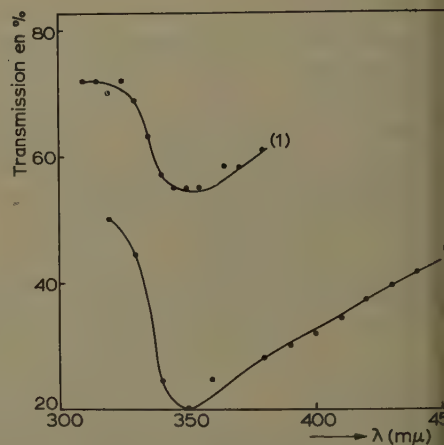


Fig. 2. Turbidimétrie du tantale et du zirconium à l'acide phénylarsonique. Courbes d'absorption en présence d'U. Courbes d'absorption: 1 = cuve de référence le „blanc et l'uranium", 100 mg U; 2 = 500 μg Ta + 100 mg U.

L'examen de ce tableau montre immédiatement que le dosage sera possible seulement dans la zone 350–370 m μ . Pour nous en convaincre, nous allons tracer les courbes de transmission en utilisant dans la cuve de référence une solution contenant tous les réactifs et 100 mg d'uranium. Nous aurons cette fois le minimum de transmission dû au zirconium ou au tantale seuls. Cette courbe ne sera pas comparable aux précédentes parce que la présence d'uranium dans la cuve de référence nous oblige à utiliser une fente beaucoup plus large (0,49 mm) (cf. Tableau II et Fig. 2).

Cette fois, le minimum de transmission est visiblement à 350 m μ . Ces conditions sont celles du dosage en présence d'uranium. On a vérifié que la courbe d'étalonnage du tantale en présence d'uranium, est superposable à celle du tantale seul, à cette longueur d'onde (Fig. 3).

TABLEAU I
COURBES DE TRANSMISSION PAR RAPPORT À L'EAU

$m\mu$	Transmission en %			
	Ta	Zr	U	U + Zr
310	46	48.5	12	12
315	44.5	48	8	8
320	44.5	47.5	5.5	5
325	45	48	4	4
330	46.5	48.5	3	3
335	47.5	50.5	2.5	3
340	49	52	4.25	3.5
345	50	53.5	13.25	9
350	51.5	58	33	24
355	53	56	50.5	27.5
360	54	57.5	48	27
365	55	58.5	53	30
370	56.5	60	50.5	29.5
375	57.5	61	51.5	30.5
380	58	62	49	29
390	60	64	31	19
400	62	66	17.5	12
410	64	67.5	10.5	8
420	66	69.5	8	7

TABLEAU II
COURBES DE TRANSMISSION PAR RAPPORT À L'URANIUM

λ $m\mu$	Transmission en %	
	50 μg Zr	300 μg Ta
310	72	
315	72	
320	70	50
325	72	
330	69	44.5
335	63	
340	57	24.5
345	55	
350	55	20
355	55	
360	55	24.5
365	58.5	
370	58.5	26
380	61.5	28
390		30
400		32
410		34.5
420		37.5
430		39.5
440		41.5
450		43

influence de l'acidité

Le domaine de précipitation du composé se situe en milieu sulfurique, à une nor-

malité comprise entre 1.2 et 3.0 *N*. Aux faibles acidités (<1.2 *N*), les petites quantités de tantale (<200 μg) ne précipitent pas. Au-delà de 3 *N*, on n'observe pas de précipité même avec 500 μg de Ta.

Ions gênants

Ce sont essentiellement le zirconium et le niobium parmi les cations; les fluorures parmi les anions.

Le zirconium: pris isolément, son domaine de précipitation en milieu sulfurique est étroit: 0.2 à 0.6 *N*. Mais en présence de tantale il y a un entraînement de Zr même à des acidités plus élevées, ainsi qu'en témoigne le Tableau III.

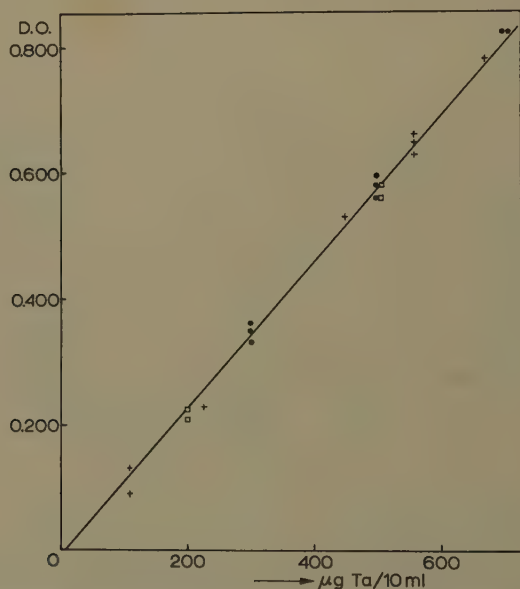


Fig. 3. Courbe d'étalonnage. Ta par turbidimétrie à l'acide phénylarsonique (milieu H_2SO_4 2 *N*, $\lambda = 350 \text{ m}\mu$; ● = Ta seul; +, □ = Ta + U.

TABLEAU III
INFLUENCE DE L'ACIDE SULFURIQUE SUR L'INTERFÉRENCE DE Zr

mg U	μg Zr	μg Ta	H_2SO_4 normalité	Densité optique	Erreur %
50	0	200	1.14	0.225	+ 2.5
50	0	200	2	0.215	— 2.5
50	50	200	1.24	0.220	0
50	100	200	1.10	0.240	+ 10
50	200	200	1.24	0.400	+ 90
50	200	200	2	0.230	+ 5
50	500	200	2	0.240	+ 10
50	500	200	2.3	0.230	+ 5

Nous considérerons qu'une erreur de 5% est dans les limites d'une méthode turbidimétrique et pouvons conclure que l'on peut tolérer un rapport moléculaire Zr/Ta 5. Par contre, il a été impossible d'éviter la coprécipitation de 1 mg de Zr (les complexants comme l'acide tartrique sont inefficaces à cette acidité; les fluorures empêchent la précipitation de Zr, mais aussi celle de Ta).

Le niobium: on utilise pour éliminer l'interférence du niobium, son complexe avec l'acide oxygénée. En prenant comme erreur relative admissible 5%, il est possible de déterminer un rapport moléculaire: Nb/Ta = 1.

DOSAGE D'UN ALLIAGE URANIUM-TANTALE DE TENEUR EN TANTALE $> 0.2\%$

Attaque

Pour 1 g d'alliage, verser 3 ml d'acide sulfurique 12 *N*, puis 5 ml d'acide nitrique concentré. Chauffer légèrement, puis ajouter goutte à goutte 0.5 ml d'acide fluorhydrique concentré jusqu'à attaque complète. Ajouter, si cela est nécessaire, un peu d'eau pour éviter la cristallisation des sels, ou de l'acide fluorhydrique si l'attaque est lente. Quand l'attaque est terminée ajouter avec précaution 14 ml d'acide sulfurique concentré et porter à fumées blanches 10 min. Laisser refroidir et selon la teneur en tantale, amener à un volume convenable.

TABLEAU IV
RÉSULTATS DE DOSAGE

Échantillon No.	Prise d'essai	Densité optique	$\mu\text{g Ta}$ dans la partie aliquote	% Ta dans l'alliage
1	400 mg alliage	0.285	250	0.62 ± 0.01
	800 mg alliage	0.565	496	
	400 mg + 91 $\mu\text{g Ta}$	0.390	342 — 91 = 251	
	400 mg + 273 $\mu\text{g Ta}$	0.595	518 — 273 = 245	
2	400 mg alliage	0.470	410	1.05 ± 0.02
	400 mg + 91 $\mu\text{g Ta}$	0.570	498 — 91 = 407	
	400 mg + 182 $\mu\text{g Ta}$	0.685	596 — 182 = 414	
3	400 mg alliage	0.340	298	0.73 ± 0.02
	200 mg alliage	0.170	149	
	400 mg + 91 $\mu\text{g Ta}$	0.445	388 — 91 = 297	
	400 mg + 182 $\mu\text{g Ta}$	0.530	462 — 182 = 280	
4	200 mg alliage	0.475	416	2.07 ± 0.04
	200 mg + 91 $\mu\text{g Ta}$	0.585	508 — 91 = 417	
	200 mg + 273 $\mu\text{g Ta}$	0.790	686 — 273 = 413	

Dosage

Prendre une partie aliquote contenant moins de 700 μg de tantale.

1. Acidifier à l'acide sulfurique (environ 1 ml de H_2SO_4 12 *N*) de telle sorte que la solution finale soit entre 2 *N* et 3 *N*. Ajouter 1 ml de H_2O_2 à 2% (s'il y a du niobium).

2. Ajouter 1 ml de la solution de glycérine, puis 1 ml de la solution d'acide phénylarsonique.

3. Préparer dans les mêmes conditions un essai à blanc avec la même quantité d'uranium (ne contenant pas de tantale) pour la cuve de référence.

4. Faire un essai sur une partie aliquote en ajoutant tous les réactifs sauf l'acide phénylarsonique. Ce deuxième essai à blanc permet de déduire les absorptions dues aux éléments formant un complexe avec H_2O_2 .

5. Faire également deux essais en ajoutant des quantités connues de tantale.

6. Après une demi-heure d'attente, déterminer la densité optique à $\lambda = 350$ m.

7. Déduire de la densité optique trouvée pour l'échantillon la somme des densités optiques dues aux deux essais à blanc.

8. Enfin, déterminer la quantité de tantale présente dans l'échantillon, d'après la droite d'étalonnage obtenue en ajoutant des quantités connues de tantale à la solution d'attaque. Cette droite doit être identique à la droite obtenue par turbidimétrie de la solution étalon de tantale.

Précision

Une teneur en tantale de 0,2 à 2% peut être déterminée avec une erreur relative $< \pm 5\%$ (cf. résultat Tableau IV).

Note

En présence de fer(III), il est nécessaire d'ajouter un peu d'acide ascorbique.

RÉSUMÉ

On décrit le dosage turbidimétrique du tantale par l'acide phénylarsonique. La méthode est rapide et nécessite rarement une séparation préliminaire. Les seuls éléments gênants sont le zirconium et le niobium, pour lesquels on peut tolérer des rapports molaires, au plus égaux à: $Nb/Ta = 1$ et $Zr/Ta = 5$.

SUMMARY

A turbidimetric method is described for the determination of tantalum with phenylarsonic acid. The method is fast and rarely requires preliminary separation. The only interfering elements are zirconium and niobium when present in molar ratios greater than $Nb : Ta = 1$ and $Zr : Ta = 5$.

ZUSAMMENFASSUNG

Beschreibung einer nephelometrischen Methode zur Bestimmung von Tantal mit Phenylarsonsäure. Die Methode ist rasch und erfordert nur in wenigen Fällen einen Trennungsprozess. Störende Elemente sind Zirkonium und Niob, wenn sie eine gewisse Konzentration überschreiten.

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THE RAPID SPECTROPHOTOMETRIC DETERMINATION OF COPPER IN NON-FERROUS ALLOYS

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INTRODUCTION

When copper determinations are required on a variety of materials such as non-ferrous alloys and corrosion products, several different methods are often employed. A survey of the literature on this subject revealed that many of the methods require rather critical reaction conditions often with specialised reagents after initial separation of the copper or of interfering elements. It was considered that many advantages could be gained if one simple method could be developed which would be applicable to a variety of alloys and materials. It was thus decided to develop a spectrophotometric method involving no separations and utilising a simple reaction to produce a self-colouring copper ion. Preliminary experiments showed that cupric chloride formation in strong hydrochloric acid solution would produce a sufficiently sensitive reaction, but this system has been little exploited and has been used by relatively few workers¹⁻⁵.

EXPERIMENTAL

Apparatus and reagents

All reagents were of the "AnalaR" quality where possible, and optical density measurements were made in glass cells on a Unicam S.P.600 spectrophotometer.

Absorption spectra

In order to assess the sensitivity of the cupric chloride system, and the types of interference likely to be met, absorption spectra were plotted for the chlorides of copper, nickel, iron, chromium and cobalt in strong hydrochloric acid solution. These spectra are reproduced in Fig. 1, and more detailed spectra for cupric chloride are shown in Fig. 2. The cupric chloride shows intense absorption at $385\text{ m}\mu$ and a less intense absorption at $950\text{ m}\mu$. The absorption characteristics of these "self-colouring" ions are summarised in Table I, from which it is obvious that minimum interference will occur with measurements at the $950\text{-m}\mu$ peak. The only serious interference likely to be met is cobalt, but this must be in appreciable amounts, and such, is not often encountered in the alloys under consideration. Measurement at the $950\text{-m}\mu$ peak enables copper concentrations down to $10\text{ }\mu\text{g/ml}$ to be determined.

TABLE I
ABSORPTION MAXIMA
 E = molecular extinction coefficient

<i>Metal</i>	$m\mu$	E	$m\mu$	E	$m\mu$	E
Cu^{+2}	385	1360	950	104		
Co^{+2}	625	354	660	531	690	572
Ni^{+2}	410	8	760	3		
Cr^{+3}	460	27	650	21		
Fe^{+3}	360	2940				

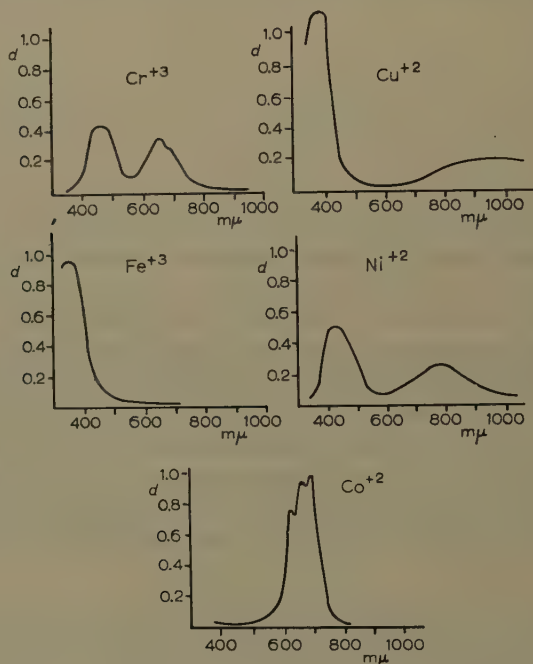


Fig. 1. Absorption spectra in concentrated HCl.

Acid concentration

The controlling factor is the hydrochloric acid concentration. The effects of this was investigated using copper concentrations from 0.125 to 5 mg/ml with appropriate cell widths to accommodate this range. The results obtained are plotted in Fig. 1. The effect of acidity is independent of copper concentration. Up to an acid concentration of 325 g hydrochloric acid per litre a rapid linear increase in absorption occurs. At concentrations above this, however, the effect is very much less pronounced. At the high acidities a variation of ± 10 g hydrochloric acid per litre produced an error in optical density reading of only ± 0.005 . To maintain errors in this range the acid concentration was controlled by sp.gr. measurement of the stock acid. The "Anala" acid has a nominal sp.gr. of 1.18 and if the stock acid is maintained between sp.gr. 1.177 and 1.184 (by hydrometer at 20°) then the concentration will be between 410 to 438 g hydrochloric acid per litre⁶. In practice it has been found that the "Anala" acid requires no adjustment.

Effects of nitric acid

Nitric acid is often employed to facilitate dissolution of many samples and it was decided to investigate the effects of this acid on the absorption of the cupric chloride. It was found that up to at least 15% by volume of concentrated nitric acid could be

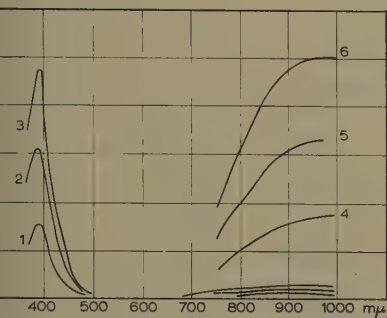


Fig. 2. Absorption spectra of cupric chloride. (1) 14 μg Cu/ml; (2) 28 μg Cu/ml; (3) 56 μg Cu/ml; (4) 200 μg Cu/ml; (5) 400 μg Cu/ml; (6) 600 μg Cu/ml.

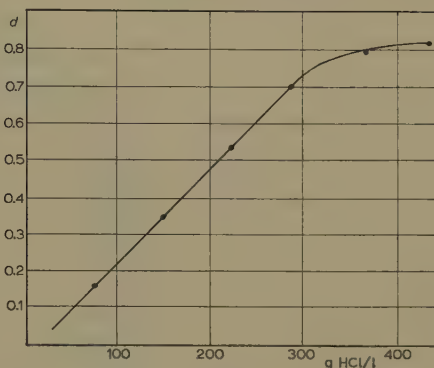


Fig. 3. Effect of acidity. Cu: 500 μg /ml; cells: 1 cm; volume: 10 ml.

tolerated in the final solution without any effects on the optical density readings. However, with this amount of nitric acid present, a continuous undesirable gas evolution occurs, and it is thus preferable to remove the bulk of any nitric acid used by a single evaporation with hydrochloric acid during processing of samples.

Stability and temperature effects

Solutions, in stoppered flasks, were stable for at least three days, and temperature changes over the range 18° to 35° had no effect on the optical density readings.

TABLE II
REPRODUCIBILITY

Cu(mg/ml)	Cell width (cm)	Mean density	Maximum deviation
0.005	4	0.040	0.001
0.05	4	0.360	0.001
0.05	1	0.088	0.002
0.1	1	0.188	0.002
0.25	1	0.446	0.005
0.5	1	0.900	0.010

Reproducibility

To check the reproducibility of preparation and measurement, known amounts of copper were processed, and optical density readings taken. The results obtained, for the samples in each case, are summarised in Table II.

The reproducibility was found to be satisfactory over a copper concentration range 50:1 and still adequate over a 100:1 range.

Effects of other elements

To test the effects of other elements, standard solutions of these were added to standard amounts of copper. In all cases the solutions were evaporated and processed to yield final solutions in concentrated hydrochloric acid. The results obtained are summarised in Table III.

TABLE III
TOLERANCE TO OTHER ELEMENTS
Cu present = 0.5 mg per ml

5%	10%	30%	50%	100%
Hg ⁺² ^a	As ⁺³ ^a	Zn ⁺²	Sb ⁺³ ^a	Al ⁺³ ^a
	Ba ⁺² ^a		Bi ⁺³	Mg ⁺² ^a
	Be ⁺² ^a		Cd ⁺²	Ni ⁺² ^a
	Ca ⁺² ^a		Cr ⁺³ ^a	Sn ⁺⁴ ^a
	Ce ⁺⁴ ^a		Mn ⁺² ^a	Fe ⁺³ ^a
	PO ₄ ⁻³ ^a		Ag ⁺¹ ^b	Pb ⁺² ^a
	TeO ₄ ⁻² ^a		Ce ⁺³ ^a	
	W ⁺⁶ ^b			
	V ⁺⁵ ^a			
	Zr ⁺² ^a			

Valencies are those as added to test solution; tolerances expressed as per cent ratio to Cu.

^a amounts greater than those shown were not investigated.

^b precipitation, but no interference occurred after centrifuging.

As a further test, calibrations were carried out using tin, lead, aluminium, zinc, magnesium, and nickel as "base metals", with copper added as standard solution. Thus, in each case 0.05 g of pure "base metal" was taken and increments of copper solution were added to cover a range up to 10% copper. In every case conformity to Beer's Law was obtained, and optical density readings reproduced within a maximum of 1.5% of the mean. Thus, for non-ferrous analysis one calibration with copper solution will suffice for a variety of alloys, e.g. tin-lead, nickel, aluminium, zinc and aluminium alloys, etc.

Calibration

The following standard solutions are suitable for calibration.

Solution 1, 1 ml \equiv 2 mg Cu. Dissolve 1 g of pure copper in a minimum of nitric acid. When dissolved evaporate to dryness. Allow to cool, then dissolve the residue in concentrated hydrochloric acid ($d = 1.18$) finally diluting to 500 ml with this acid.

Solution 2, 1 ml \equiv 0.2 mg Cu. Dilute 50 ml of solution 1 to 500 ml with concentrated hydrochloric acid ($d = 1.18$). Calibration data, using these solutions, are given in Tables IV and V. Table IV shows the ranges and dilutions etc. and then reference to Table V gives the additions of standard copper solutions together with the equivalent copper contents.

In all cases measure the required volume of standard copper solution into 20-, 50- or 100-ml graduated flasks, as appropriate, and dilute to volume with concentrated hydrochloric acid ($d = 1.18$). Measure the optical densities of these solutions at 95 m μ in the appropriate cells and plot density against % Cu, when linear calibration should be obtained.

TABLE IV

	A	B	C	D	E
Cu content (%)	0-2	to 5	to 10	to 50	to 100
Sample wt. (g)	0.1	0.05	0.05	0.05	0.05
Final vol. (ml)	20	20	50	50	100
Cell width (cm)	4	4	4	1	1
Copper soln. No.	2	2	2	1	1

TABLE V

ml OF STANDARD Cu SOLUTION AND CORRESPONDING %Cu

A		B		C		D		E	
ml	% Cu	ml	% Cu	ml	% Cu	ml	% Cu	ml	% Cu
2	0.4	2.5	1	5	2	2.5	10	5	20
4	0.8	5.0	2	10	4	5.0	20	10	40
6	1.2	7.5	3	15	6	7.5	30	15	60
8	1.6	10.0	4	20	8	10.0	40	20	80
10	2.0	12.5	5	25	10	12.5	50	25	100

Analytical procedure

As a result of the investigations carried out, the following procedure has been established for the determination of copper in samples of alloys, etc. Since the method is applicable to a wide variety of samples, individual treatment for dissolution can be varied, but the following method can be taken as being typical. The sample weights, final volumes and cell widths to cover different ranges of copper contents can be chosen from Table IV.

Transfer the sample to a 100-ml beaker, and attack with hydrochloric acid, added dropwise. Complete the dissolution of the sample by addition of concentrated nitric acid. Evaporate to dryness, taking care to avoid baking. Allow the residue to cool, then dissolve, in the cold, in about 5 ml of concentrated hydrochloric acid ($d = 1.18$). If any insoluble compounds appear, transfer to a centrifuge tube, washing with a minimum of cold concentrated hydrochloric acid. Spin off insoluble matter, then decant and wash the solution to the required standard volume with the hydrochloric acid. Measure the optical density of the solution at 950 m μ using the hydrochloric acid as compensating solution. Calculate the copper content of the sample by reference to the calibration curves.

Accuracy

The accuracy of the method was checked by analysing several British Chemical Standard samples, the results obtained being summarised in Table VI. These results showed that both accuracy and reproducibility are quite adequate.

DISCUSSION

The procedure which has been evolved is very simple, and shows many advantages over other methods using somewhat specialised reagents. Many different types of samples have been analysed by this method in this laboratory, including non-ferrous alloys on a control basis and corrosion and breakdown deposits. One advantage in dealing with corrosion products, etc. is that the reaction is sufficiently sensitive to enable a small sample to be used, and at the same time the final solution is not con-

TABLE VI
RESULTS ON STANDARD SAMPLES
British Chemical Standards (B.C.S.) used

Standard	Certified % Cu	% Cu found Mean of 10	Standard deviation	Coefficient of variation
White metal 'A'	0.33	0.35	± 0.008	± 2.3
White metal 'B'	4.08	4.13	± 0.067	± 1.6
Cupro nickel "A"	68.76	68.3	± 1.06	± 1.5
Mn brass "B"	58.9	58.4	± 1.55	± 2.7
Al alloy 181	4.64	4.73	± 0.033	± 0.7
Mg/Al alloy	0.13	0.14	± 0.024	± 17.1

taminated with reagents. Thus, after evaporation of excess acid, further analyses can be carried out on the same solution. Although satisfactory results have been obtained on samples of high copper contents, the method is not recommended where copper is the major constituent. In such cases a differential spectrophotometric technique using perchloric acid is used. However, the method does enable rapid classification to be made in such cases. With some samples, precipitation of insoluble compounds such as silica, tungsten oxide, silver chloride, etc. occurs, but no errors have been observed when these have been removed by centrifuging and washing with concentrated hydrochloric acid.

Although relatively large amounts of iron do not interfere, it has been found that the method is not directly applicable to the determination of copper in iron and steels. For these samples the reaction with diquinolyl followed by amyl alcohol extraction is used. As an indication of the sensitivity of the simple chloride reaction a copper concentration of 10 μg per ml can be measured at 950 $\text{m}\mu$. On the Unicam S.P. 600 instrument this produces an optical density of approximately 0.1 when using a 4-cm cell.

ACKNOWLEDGEMENT

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SUMMARY

A very simple method has been established for the rapid determination of copper, employing formation of the chlorocupric anion by means of concentrated hydrochloric acid. The absorbance of the chlorocupric anion is measured spectrophotometrically at a wavelength of 950 $\text{m}\mu$. The method is applicable to a wide variety of samples, including many non-ferrous alloys.

RÉSUMÉ

Une méthode spectrophotométrique, rapide et très simple, est proposée pour le dosage du cuivre dans divers alliages. On utilise l'acide chlorhydrique comme réactif et on mesure l'absorption de l'anion chlorocuprique formé.

ZUSAMMENFASSUNG

Beschreibung einer raschen und einfachen spektrophotometrischen Methode zur Bestimmung von Kupfer. Sie beruht auf der Messung der Absorption des Chlorokupfer Anions.

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THE SPECTROPHOTOMETRIC DETERMINATION OF MICROGRAM AMOUNTS OF CERIUM

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The majority of methods available for the colorimetric determination of cerium depend on the oxidising properties or colour of ceric solutions. Cerous ion can be oxidised to persulphate in hot acidic solution in the presence of catalytic amounts of silver ion. The yellow colour of the resulting ceric solution is sufficiently intense for the determination of milligram amounts of cerium¹⁻³. A rather more sensitive procedure depends on the yellow colour which is formed when a cerous salt is treated with potassium persulfate in the presence of air or hydrogen peroxide⁴⁻⁶. In acid solution, ceric ion oxidises a number of organic compounds, such as brucine⁷, sulphanilic acid⁸, benzi-^{9,10}, and the leucobase of malachite green¹¹, to coloured compounds which can be used for the photometric determination of the element.

GORDON AND FEIBUSH¹² have described an indirect method for the determination of cerium, in which ceric ion, formed by oxidation with lead dioxide, was treated with excess ferrous sulphate solution; excess ferrous ion remaining was determined photometrically with 1,10-phenanthroline. When this method was tested using microgram amounts of cerium very variable results were obtained; this variability was attributed to the difficulty of completely removing traces of suspended lead dioxide from the solution and to oxidation of ferrous ion before addition of the complexing agent. Attempts were therefore made to oxidise the cerous ion by means of persulphate in the presence of silver ion as catalyst. It was found that complete oxidation of up to 100 μg of Ce^{+3} in 4 ml of 0.3 *N* sulphuric acid occurred when the solution was heated in a boiling water bath for 5 min with 1 ml of 0.2% ammonium persulphate, in the presence of 50 μg of silver ion (added as silver sulphate). Under these conditions excess persulphate was completely decomposed in 5-7 min. If the solution was boiled on a hot plate oxidation of cerium was incomplete.

SANDELL¹³ has suggested that ceric-cerium could be estimated by treating the sample with excess of a solution of the red ferrous-phenanthroline complex. The increase in optical density of the solution, caused by the oxidation of the ferrous complex to the faintly coloured ferric-phenanthroline complex, would be an indirect measure of the cerium present. In this method the ferrous iron added would be stabilised by the phenanthroline. It would therefore be less likely to be oxidised by the

* This work was carried out in partial fulfillment of the requirements for the degree of Ph.D. (London).

oxygen, with which the solution is super-saturated, than if the ferrous solution was added separately as described by GORDON AND FEIBUSH¹².

The ferrous-phenanthroline complex is completely stable over the pH range 2–9. At pH values below 2, the complex is partly decomposed and its colour is much weaker. When ferrous-phenanthroline reagent was added to a blank solution which had been treated with persulphate as described above, the low pH of the resultant solution (<1) caused rapid fading of the colour. Since cerous hydroxide precipitates at pH 2.5, the range usable for the determination of cerium is limited to pH 2.0–2.5. It was found that if the solution was buffered to pH 2.3 with sodium acetate, the colour was stable for about 1 h.

The sensitivity of the method can be doubled if sulphonated bathophenanthroline is substituted for phenanthroline in the reagent.

DETERMINATION OF CERIUM

Reagents

Silver sulphate solution (100 $\mu\text{g Ag}^+/\text{ml}$). Prepare a solution containing 0.1445 g silver sulphate per l.

Ammonium persulphate solution. Dissolve 1 g of ammonium persulphate in 50 ml of water. Since this reagent is unstable it should be prepared freshly immediately before use.

Ferrous-phenanthroline reagent. Dissolve 1.0 g of 1,10-phenanthroline and 0.0653 g of ferrous ammonium sulphate in 250 ml of 0.1 N sulphuric acid. This solution has an optical density of ca. 7.0 at 510 m μ in a 1-cm cell and 1 ml contains 37.2 μg of Fe²⁺ which is equivalent to ca. 93 μg of Ce⁺⁴. This reagent contains a ninefold excess of phenanthroline over the amount required to combine with the ferrous ion present.

Sodium acetate (4.5 M). Dissolve 153 g of sodium acetate trihydrate in water and dilute to 250 ml.

Standard cerium solution. Digest 0.1228 g of pure cerium dioxide overnight with 10 ml of concentrated sulphuric acid at 270°. Dilute with 100 ml of water and add 0.5 ml of 30% hydrogen peroxide. Boil until all the solid has dissolved and excess hydrogen peroxide has been destroyed. When cold, dilute to 250 ml. This stock solution contains 400 $\mu\text{g Ce}^{+3}/\text{ml}$. Prepare a working solution containing 10 $\mu\text{g Ce}^{+3}/\text{ml}$ from it as required.

Method

Pipette into a 25-ml conical flask 4 ml of the solution to be analysed (containing not more than 80 μg of cerium, and having an acidity not greater than 0.1 M). Add 0.13 ml of concentrated sulphuric acid (s.g. 1.84), 0.5 ml of silver sulphate and 1 ml of ammonium persulphate solution. Immerse the flask to about half its height in a bath of boiling water for 10 min. After cooling, transfer the solution to a 10-ml graduated flask, using not more than 2 ml of water for washing out the conical flask. Add 1 ml of ferrous-phenanthroline reagent followed by 1 ml of 4.5 M sodium acetate solution. Mix well and dilute to 10 ml with water. Measure the optical density of the solution at 510 m μ in a 1-cm cell within 30 min of mixing. Carry out a blank determination in the same manner, using 4 ml of water instead of the sample. Calibrate the method using 4 ml of the dilute standard cerium solution (40 $\mu\text{g Ce}^{+3}$).

Calibration curve and reproducibility

The linearity of the calibration curve was checked by treating various amounts of cerous sulphate as described above. The results are given in Table I and show that the decrease in optical density of the solutions as compared with the blank is proportional to the weight of cerium up to about 80 μg .

TABLE I

CALIBRATION OF METHOD WITH KNOWN AMOUNTS OF CERIUM

Wt. of Ce (μg)	Optical density ^a	Mean decrease in optical density	Decrease per 10 μg Ce
0	0.741 0.739 0.602		
20	0.602 0.458	0.138	0.0690
40	0.458	0.282	0.0705
50	0.387 0.385 0.318	0.354	0.0708
60	0.316 0.158	0.423	0.0705
80	0.147	0.582	0.0727

^a at 510 $\text{m}\mu$, 1-cm cell

In order to test the reproducibility of the method replicate determinations were carried out on 50- μg samples of cerium. The following optical density decreases were observed: 0.350, 0.360, 0.352, 0.344, 0.364, 0.359; mean 0.355; standard deviation 0.007; coefficient of variation 2.0%.

Interference of foreign ions

The interference of a number of ions was investigated by carrying out the persulphate oxidation stage on them and then treating with ferrous-phenanthroline reagent as described above. The following ions were found to cause no interference: Pb^{+2} , Na^{+} , K^{+} , Ca^{+2} , Mg^{+2} (20 mg of each), Al^{+3} , Fe^{+3} , Ti^{+4} (10 mg of each), Ag^{+} , Be^{+2} , Mn^{+2} , Co^{+2} , Cu^{+2} , Hg^{+2} , Ni^{+2} , Zn^{+2} , MoO_4^{-2} , ReO_4^{-} , SeO_4^{-2} , TeO_4^{-2} (1 mg of each), La^{+3} (200 μg), Gd^{+3} , Ge^{+4} , In^{+3} , La^{+3} , Sc^{+3} , Tl^{+} , UO_2^{+2} (100 μg of each).

Serious interference is experienced with ions which can either oxidise the ferrous-phenanthroline reagent directly, or which can be oxidised by persulphate to strong oxidising agents. Traces of chromium and manganese must be absent since they are oxidised by persulphate to chromate and permanganate respectively. Chromium can be removed by volatilisation as chromyl chloride; manganese is most conveniently separated by ion exchange¹⁵. Vanadate also interferes slightly; 1 mg of VO_3^{-} is equivalent to *ca.* 14 μg of cerium.

Chloride, oxalate, citrate and tartrate interfere by reducing the ceric salt. Considerable interference is caused by fluoride which bleaches the ferrous-phenanthroline complex. The presence of even traces of perchlorate leads to cloudiness of the solution owing to the precipitation of slightly soluble phenanthroline perchlorate. If any of

these interfering anions are present in the solution to be analysed they should be removed by fuming to dryness twice with concentrated sulphuric acid.

SUMMARY

A spectrophotometric procedure, which has a coefficient of variation of ca. 2%, is described for the determination of up to 80 μg of cerium. Ceric ion formed by oxidation with persulphate, in the presence of catalytic amounts of silver, is reduced to the cerous state by treatment with excess ferrous-phenanthroline reagent. The decrease in optical density of the ferrous-phenanthroline compared with the reagent blank is a measure of the amount of cerium present. The only common cations which cause serious interference are Mn^{+2} and Cr^{+3} .

RÉSUMÉ

Une méthode spectrophotométrique est proposée pour le dosage du cérium. On procède par oxydation du cérium au moyen de persulfate, en présence d'argent comme catalyseur. Puis on traite la solution à analyser par la phénanthroline ferreuse et on mesure la diminution de la densité optique, en comparant à un essai à blanc.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung von Cerium. Ce(IV) wird mit einem Überschuss von Eisen(II)-Phenanthrolin reduziert und die Abnahme der optischen Dichte der Eisen(II)-Phenanthrolinlösung gemessen.

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DOSAGE DE L'ACIDE TARTRIQUE ET DES TARTRATES PAR LE TÉTRACÉTATE DE PLOMB

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(Reçu le 17 juin 1960)

Pour le dosage oxydimétrique de l'acide tartrique on se sert d'agents oxydants ergiques comme par exemple le permanganate alcalin¹⁻³, les composés du cérium trivalent⁴⁻⁶, le bichromate^{7,8}, l'iodate^{9,10}, le periodate^{11,12}, le vanadate¹³⁻¹⁶ ou en de composés de cuivre trivalent^{17,18}. Dans la plupart des cas, il est nécessaire ajouter un excès de réactif et de chauffer, plus ou moins longtemps.

Lors de notre étude, nous avons constaté que l'oxydation de l'acide tartrique par tétracétate de plomb s'effectue à la température du laboratoire, en présence acétate alcalin, en milieu d'acide acétique à 80%, rapidement et quantitativement ec formation d'anhydride carbonique et d'eau.

Nous avons pu fixer la durée d'action à 30 min en utilisant un excès de réactif. La antité non utilisée de tétracétate de plomb est déterminée par un titrage potentio-étrie au moyen d'une solution d'hydroquinone. Ces deux solutions (tétracétate plomb et hydroquinone) sont très stables. La vitesse, la précision et même la plicité d'exécution du procédé proposé dépassent celles de la plupart des méthodes ydimétriques utilisées jusqu'à présent.

PARTIE EXPÉRIMENTALE

actifs

Acide sulfurique, acide acétique, acétate de potassium, tartrate double de sodium de potassium, tartrate acide de potassium (p.a. Merck, Lachema).

$\text{Na}_5\text{Bi}(\text{C}_4\text{H}_2\text{O}_6)_2 \cdot 9\text{H}_2\text{O}$, $\text{Na}_5\text{Bi}(\text{C}_4\text{H}_2\text{O}_6)_2 \cdot 6\text{H}_2\text{O}$, $\text{K}_5\text{Bi}(\text{C}_4\text{H}_2\text{O}_6)_2 \cdot 4\text{H}_2\text{O}$,

$\text{Bi}(\text{C}_4\text{H}_2\text{O}_6)_2 \cdot 8\text{H}_2\text{O}$ et $\text{BiC}_8\text{H}_9\text{O}_{12}$ ont été préparés au laboratoire*.

Solution d'acide tartrique 0.005 M, titrée par le periodate de potassium¹². Solution tétracétate de plomb 0.05 M dans l'acide acétique glacial (exempt de plomb(II)), éparée à partir de minium et d'acide acétique glacial¹⁹ et titrée potentiométrique-ent par une solution étalon d'hydroquinone²⁰.

Solution d'hydroquinone dans l'acide sulfurique à 1%, titrée par le bichromate deassium.

pareils

Les titrages potentiométriques ont été effectués au moyen d'un pH-mètre AK ovodružba, Praha), en utilisant un fil de platine comme électrode indicatrice et

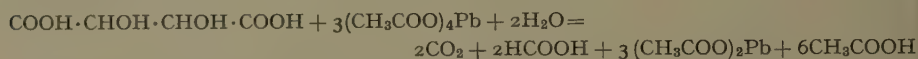
Nous exprimons notre gratitude à M. B. STRAUCH de l'Institut de chimie inorganique de niversité Charles à Prague, qui a mis à notre disposition les composés cités.

une électrode au calomel comme électrode de référence. Pour agiter le liquide, agitateur électromagnétique a été utilisé. Les titrages ont été effectués à l'aide microburettes de 5 ml (graduées en 0.01 ml).

RÉSULTATS

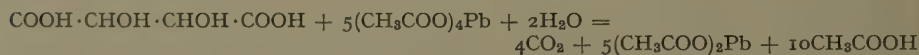
Dans nos travaux précédents, concernant la comparaison de l'effet oxydant du tétracétate de plomb ainsi que de l'acide périodique et de ses sels^{12,19-22}, nous avons examiné, entre autre, la possibilité d'utiliser les réactions du tétracétate de plomb solution aqueuse et en solution dans des acides dilués, à des fins analytiques. Nous avons constaté qu'il est possible de doser, dans les conditions données, l'hydrazine ses dérivés, par titrage potentiométrique direct, au moyen de tétracétate de plomb de même que l'acide ascorbique²¹ et quelques ions inorganiques courants (Cr^{+2} , Ti^{+3} , Fe^{+2} , Sn^{+2} , Sb^{+3} , As^{+3}).

Le dosage de l'acide tartrique par titrage potentiométrique direct²⁰, d'après l'équation



est rendu difficile par l'oxydation subséquente de l'acide formique produit. Pour cette raison, le dosage d'autres substances organiques par le tétracétate de plomb est moins favorable que, par exemple, par l'acide périodique.

Nous nous sommes efforcés par conséquent de trouver les conditions nécessaires pour obtenir une oxydation quantitative de l'acide tartrique en anhydride carbonique et eau:



D'après les indications de la littérature, l'oxydation de l'acide formique, ne s'effectuant que lentement en milieu d'acide acétique²³, peut être accélérée par la présence d'eau²⁴ et d'acétates alcalins²⁵. C'est pourquoi nous avons étudié d'abord l'influence de l'eau ainsi que celle des acétates (alcalins) sur la rapidité d'oxydation de l'acide tartrique: A 10.00 ml de solution d'acide tartrique 0.005 *M* dans l'acide acétique glacial, il a été ajouté une quantité variable d'eau et d'acétate de potassium, 10.00 ml de solution de PbAc_4 0.05 *M* (excédent double, comparé à l'oxydation quantitative d'après l'équation (2)) et l'acide acétique glacial jusqu'à un volume total de 30 ml. On laisse reposer la solution pendant 10 min; la quantité de PbAc_4 qui n'a pas réagi est ensuite déterminée par titrage potentiométrique au moyen d'une solution d'hydroquinone 0.05 *M*. (Pendant le titrage, la solution se trouble par formation de sulfure de plomb, provenant de la réaction des ions Pb^{+2} avec l'acide sulfurique, ajouté à la solution d'hydroquinone pour augmenter sa stabilité). On effectue parallèlement un essai à blanc; la différence des volumes utilisés permet de calculer la quantité de PbAc_4 , nécessaire à l'oxydation de l'acide tartrique. Les résultats sont donnés dans le Tableau I.

Nous avons constaté que la quantité de réactif consommée était la même après 6 h qu'après 10 min. (Milieu acide acétique à 80% + 5 g d'acétate de potassium). En effectuant l'oxydation dans des solutions plus diluées d'acide acétique (par exemple, acide acétique à 50%), il se produit une hydrolyse partielle du réactif après 20 min.

TABLEAU I

oxydation de l'acide tartrique par le tétracétate de plomb dans des milieux différents, après 10 min

Milieu	Consommation de mols de $PbAc_4$ /x mol d'acide tartrique
Acide acétique glacial	1.03
Acide acétique 80%	3.04
Acide acétique 80% + 0.04 g d'acétate de potassium	3.32
Acide acétique 80% + 0.4 g d'acétate de potassium	4.26
Acide acétique 80% + 1 g d'acétate de potassium	4.88
Acide acétique 80% + 5 g d'acétate de potassium	5.01

viron, ce qui n'est pas le cas avec l'acide acétique à 80%, même après un temps relativement long. Nous avons finalement ramené la quantité d'acétate de potassium à 0.04 g, la réaction étant alors suffisamment rapide.

Nous avons ensuite déterminé la rapidité d'oxydation de l'acide tartrique par $PbAc_4$ dans ces conditions, en ajoutant à 10.00 ml de la solution d'acide tartrique 0.05 *M* dans l'acide acétique glacial), 5 ml de la solution aqueuse d'acétate de potassium à 20% et 10.00 ml de la solution de tétracétate de plomb 0.05 *M* et en titrant après un certain temps, l'excès de réactif par la solution d'hydroquinone 0.05 *M*. Il a été effectué parallèlement un essai à blanc permettant de déterminer par différence la quantité consommée de $PbAc_4$ pour l'oxydation de l'acide tartrique. Les résultats obtenus sont donnés dans le Tableau II.

TABLEAU II

oxydation de l'acide tartrique par le tétracétate de plomb, en excès, en fonction du temps

Temps en min	Consommation des mols de $PbAc_4$ /x mol d'acide tartrique
2	3.76
5	4.40
10	4.87
20	5.00
30	5.00
45	5.02
240	4.99
360	5.00

Méthode opératoire

La prise d'essai correspondante à 5 ml env. d'acide tartrique 0.01 *M* (ou la quantité correspondante du tartrate examiné) est diluée, soit: (a) dans 5 ml d'eau, (b) dans 5 ml d'acide acétique glacial, (c) dans 5 ml de la solution aqueuse d'acétate de potassium de 20%. On ajoute 10 ml de solution d'acétate de potassium à 10% dans l'acide acétique glacial (a), ou 5 ml de la solution aqueuse d'acétate de potassium à 20% (b), ou 10 ml d'acide acétique glacial (c). Finalement, on ajoute 10.00 ml de la solution de $PbAc_4$ 0.05 *M*. Après 30 min, la quantité de $PbAc_4$ non consommée est déterminée par titrage potentiométrique au moyen d'une solution d'hydroquinone

0.05 *M*. On exécute parallèlement un essai à blanc et, de la différence des quantités consommées, on peut calculer la teneur de la substance à doser.

1 ml de PbAc₄ 0.05 *M* (= 1 ml d'hydroquinone 0.05 *M*) correspond à 1.5009 mg d'acide tartrique. La différence décisive de la méthode est de 0.18%.

On a pu ainsi déterminer la teneur en tartrate des composés suivants: KNaC₄H₄O₆ · 4H₂O, KC₄H₅O₆, Na₅Bi(C₄H₂O₆)₂ · 9H₂O, Na₅Bi(C₄H₂O₆)₂ · 6H₂O, K₅Bi(C₄H₂O₆)₂ · 4H₂O, LiBi(C₄H₂O₆)₂ · 8H₂O et BiC₈H₉O₁₂. Tous ces tartrates sont facilement solubles dans l'eau, excepté BiC₈H₉O₁₂, qu'on peut dissoudre à chaud dans une solution d'acétate de potassium à 20%.

RÉSUMÉ

En milieu d'acide acétique à 80%, en présence d'acétate de potassium, l'oxydation de l'acide tartrique par le tétracétate de plomb s'effectue quantitativement. Lors du dosage volumétrique indirect de l'acide tartrique et des tartrates, on ajoute un excès de PbAc₄; après 30 min, cet excès est déterminé par titrage potentiométrique à l'aide d'une solution d'hydroquinone.

SUMMARY

It was found, that in a medium of 80% acetic acid, in the presence of potassium acetate the oxidation of tartaric acid by lead(IV)-acetate takes place quantitatively. In the indirect determination of tartaric acid and tartrates, an excess of lead(IV)-acetate is used, allowing 30 min for the reaction to take place. The remaining reagent is then determined by potentiometric titration with a volumetric hydroquinone solution.

ZUSAMMENFASSUNG

Beschreibung einer indirekten Methode zur Bestimmung von Weinsäure und Tartraten durch Oxydation mit Blei-(IV)-acetat. Der Überschuss an Blei-(IV)-acetat wird mit einer Hydrochinonlösung potentiometrisch titriert. Der quantitative Verlauf der Oxydation wird nachgewiesen.

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METHOD FOR DETERMINATION OF THE EQUIVALENCE POINT IN
POTENTIOMETRIC TITRATIONS

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INTRODUCTION

In the literature a number of methods are described for determination of the equivalence point in potentiometric titrations. It is clear that if the equivalence point and inflection point of the potential-volume curve coincide, the end-point is reached when the second derivative is zero.

KOLTHOFF¹⁻³ and other authors⁴⁻⁶, however, regard the zero value of the second derivative as the end-point of the titration. This may lead to inaccurate results, as has been shown by HAHN⁷⁻⁹.

In addition several methods of graphical determination of the inflection point have been proposed in the literature, *e.g.* TUBBS' concentric-arcs method¹⁰, which has no theoretical basis, GRAN's method¹¹ of transformed titration curves and the method 'equal areas' described by KOHN AND ZITKO¹². These methods require a graphical representation of the experimental results and a visual evaluation of the end-point.

HAHN⁹ published a method of calculation which yields accurate results but its application is limited.

We have developed an accurate method which can be applied more generally to potentiometric titrations when a graph as shown in Fig. 7 is available. The method is simple, requires no graphical representation of the experimental results and possesses a theoretical basis. In addition it gives approximate values for the dissociation constant of the slightly dissociated substance formed during the titration. The theory of the method is outlined below.

THEORY

An equation of a symmetric potential-volume curve will be derived and the differences between potentials corresponding to equidistant volumes near the end-point will be calculated. Further it will be shown that ratios between the differences mentioned are functions of two parameters which determine the end-point and the ionization constant respectively.

In addition, the influence of dilution on the two parameters will be studied.

List of symbols used

Symbol	Meaning	Dimension
K	ionization constant	mmol ² ml
$[A]$	concentration of A	mmol ml
t	titre of the reagent	mmol ml
v	volume of the reagent added	ml
V	initial volume of the solution to be titrated	ml
v_0	volume of the reagent added at the equivalence point	ml
pA	$-\log A$	—
pK	$-\log K$	—
e	base of natural system of logarithms	—
E	electromotive force of a cell	mV
E_0	electromotive force with $[A] = 1$ mmol/ml	mV
F	Faraday constant (96,500)	C mol
α	constant	mV
β	constant ($= RT/F$)	mV
R	gas constant ($= 8.315$)	mV C deg ⁻¹ mol
T	absolute temperature	deg
$\varrho, \varrho_a, \varrho_b$	parameters determining the equivalence point	—
$\varrho_K, \varrho_H, \varrho_F$	ϱ -values found by Kolthoff's, Hahn's and our method respectively	—
$\kappa, \kappa_a, \kappa_b$	parameters determining the ionization constant ($\kappa = \sqrt{K}/t\varphi$)	—
$\varphi, \varphi_a, \varphi_b$	parameters determining the dilution ($\varphi = \Delta v/V_c$)	—
$\tau_0 \tau_1 \tau_2 \tau_3$	potential steps of fixed order	mV
$\Delta_0 \Delta_1 \Delta_2 \Delta_3$	potential steps of decreasing order	mV
Δv	volumes added during the titration	ml
$E_a E_b E_c$	potentials between the steps τ_0 and τ_1	mV
$v_a v_b v_c$	volumes added at the potentials $E_a E_b E_c$ respectively	ml
$V_a V_b V_c$	volumes of the solution being titrated at the potentials E_a, E_b and E_c respectively	ml
j, n	integers	—
Z	function of the parameters ϱ, κ and φ	—
$r_1 r_2 r_3$	ratios of potential steps of fixed order ($r_j = \tau_j/\tau_{j-1}$)	—
$R_1 R_2 R_3$	ratios of potential steps of decreasing order ($R_j = \Delta_j/\Delta_{j-1}$)	—

Derivation of a general expression for the potentiometric titration curve of the system
 $A + D \rightarrow AD$

If a strong electrolyte AB is titrated with another strong electrolyte CD to form a slightly dissociated substance AD with an ionization constant K , the following equations apply:

$$[A] \cdot [D] = K$$

$$[B] = \frac{tv_0}{V + v}$$

$$[C] = \frac{tv}{V + v} \quad (3)$$

$$[A] + [C] = [B] + [D] \quad (4)$$

These equations yield:

$$\frac{\sqrt{K}}{[A]} - \frac{[A]}{\sqrt{K}} = \frac{t(v - v_0)}{\sqrt{K}(V + v)} \quad (5)$$

with

$$pA = -\log [A] \quad (6)$$

and

$$pK = -\log K \quad (7)$$

It follows that:

$$\frac{\sqrt{K}}{[A]} - \frac{[A]}{\sqrt{K}} = \exp \left\{ \ln \frac{\sqrt{K}}{[A]} \right\} - \exp \left\{ -\ln \frac{\sqrt{K}}{[A]} \right\} = 2 \sinh \left(\frac{pA - \frac{1}{2}pK}{\log e} \right) \quad (8)$$

Combination of (5) and (8) and resolution of the equation for pA, gives

$$pA = \frac{1}{2}pK + (\log e) \sinh^{-1} \frac{t(v - v_0)}{2\sqrt{K}(V + v)} \quad (9)^*$$

The electromotive force of a cell can be calculated from

$$E = E_0 - \frac{RT}{F} \ln [A] \quad (10)$$

Substitution of (6) in (10) gives

$$E = E_0 + \frac{RT}{F \log e} pA \quad (11)$$

Substitution of (9) in (11) gives

$$E = E_0 + \frac{RT}{2F \log e} pK + \frac{RT}{F} \sinh^{-1} \left\{ \frac{t(v - v_0)}{2\sqrt{K}(V + v)} \right\} \quad (12)$$

This formula can be considered as the general equation of the potential-volume curve for the system mentioned above.

At the temperature T the values:

$$\alpha = E_0 + \frac{RT}{2F \log e} pK \quad \text{and} \quad \beta = \frac{RT}{F} \quad (13)$$

$y = \sinh^{-1} x$, if $x = \sinh y = (e^y - e^{-y})/2$

are constants. Consequently,

$$E = \alpha + \beta \sinh^{-1} \frac{t(v - v_0)}{2\sqrt{K(V + v)}}$$

and after the j -th addition:

$$E_j = \alpha + \beta Z_j$$

where

$$Z_j = \sinh^{-1} \frac{t(v_j - v_0)}{2\sqrt{K(V + v_j)}}$$

Determination of the equivalence point

Case a

A titration curve of the type represented in Fig. 1a can be obtained when a solution is titrated with equal increments Δv of a reagent. The volume v_a corresponds to the potential E_a between the steps τ_1 and τ_0 . The volume v_0 at the equivalence point is determined by the equation:

$$v_0 = v_a + \varrho_a \Delta v \quad (17a)$$

Consequently, v_0 can be calculated if ϱ_a is known. In the next section a method will be developed for obtaining ϱ_a -values ($0 \leq \varrho_a \leq 0.50$).

Case b

A titration curve of the type represented in Fig. 1b can be obtained when solution is titrated with equal increments Δv of a reagent. The volume v_b corresponds to the potential E_b between the steps τ_0 and τ_1 . The volume v_0 at the equivalence point is determined by the equation:

$$v_0 = v_b - \varrho_b \Delta v \quad (17b)$$

Consequently, v_0 can be calculated if ϱ_b is known. In the next section a method will be developed for obtaining ϱ_b -values ($0 \leq \varrho_b \leq 0.50$).

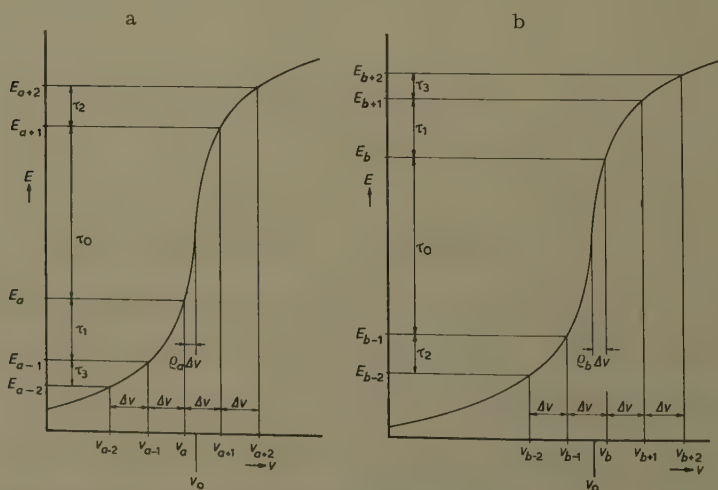


Fig. 1. Symmetric potential-volume curves (effect of dilution neglected; $\varphi = 0$).

etermination of the parameters ρ and κ

The ratios of potential steps are independent of α and β (see eqn. 14). Defining the r_j of the potential steps τ_j and τ_{j-1} as:

$$r_j = \frac{\tau_j}{\tau_{j-1}}$$

get:

from Fig. 1a and eqn. (15):

$$\left. \begin{aligned} r_1 &= \frac{\tau_1}{\tau_0} = \frac{Z_a - Z_{a-1}}{Z_{a+1} - Z_a} \\ r_2 &= \frac{\tau_2}{\tau_1} = \frac{Z_{a+2} - Z_{a+1}}{Z_a - Z_{a-1}} \\ r_3 &= \frac{\tau_3}{\tau_2} = \frac{Z_{a-1} - Z_{a-2}}{Z_{a+2} - Z_{a+1}} \end{aligned} \right\} \quad (18a)$$

th: $\left. \begin{aligned} v_j &= j \cdot \Delta v \\ v_a &= a \cdot \Delta v \end{aligned} \right\} \quad (19a)$

$$\left. \begin{aligned} V_a &= V + v_a \\ \varphi_a &= \frac{\Delta v}{V_a} \\ \kappa_a &= \frac{\sqrt{K}}{t\varphi_a} \end{aligned} \right\} \quad (20a)$$

from Fig. 1b and eqn. (15):

$$\left. \begin{aligned} r_1 &= \frac{\tau_1}{\tau_0} = \frac{Z_{b+1} - Z_b}{Z_b - Z_{b-1}} \\ r_2 &= \frac{\tau_2}{\tau_1} = \frac{Z_{b-1} - Z_{b-2}}{Z_{b+1} - Z_b} \\ r_3 &= \frac{\tau_3}{\tau_2} = \frac{Z_{b+2} - Z_{b+1}}{Z_{b-1} - Z_{b-2}} \end{aligned} \right\} \quad (18b)$$

With: $\left. \begin{aligned} v_j &= j \cdot \Delta v \\ v_b &= b \cdot \Delta v \end{aligned} \right\} \quad (19b)$

$$\left. \begin{aligned} V_b &= V + v_b \\ \varphi_b &= \frac{\Delta v}{V_b} \\ \kappa_b &= \frac{\sqrt{K}}{t\varphi_b} \end{aligned} \right\} \quad (20b)$$

follows from eqns. (16) and (17a) that:

$$Z_{a+n} = \sinh^{-1} \left\{ \frac{(n - \rho_a)}{2\kappa_a(1 + n\varphi_a)} \right\} \quad (21a)$$

it follows from eqns. (16) and (17b) that:

$$Z_{b+n} = \sinh^{-1} \left\{ \frac{(n + \rho_b)}{2\kappa_b(1 + n\varphi_b)} \right\} \quad (21b)$$

stitution of (21a) in (18a) gives the equations

$$\left. \begin{aligned} r_1 &= \frac{\sinh^{-1} \left\{ \frac{1 + \rho_a}{2\kappa_a(1 - \varphi_a)} \right\} - \sinh^{-1} \left\{ \frac{\rho_a}{2\kappa_a} \right\}}{\sinh^{-1} \left\{ \frac{1 - \rho_a}{2\kappa_a(1 + \varphi_a)} \right\} + \sinh^{-1} \left\{ \frac{\rho_a}{2\kappa_a} \right\}} \\ r_2 &= \frac{\sinh^{-1} \frac{2 - \rho_a}{2\kappa_a(1 + 2\varphi_a)} - \sinh^{-1} \frac{1 - \rho_a}{2\kappa_a(1 + \varphi_a)}}{\sinh^{-1} \left\{ \frac{1 + \rho_a}{2\kappa_a(1 - \varphi_a)} \right\} - \sinh^{-1} \left\{ \frac{\rho_a}{2\kappa_a} \right\}} \\ r_3 &= \frac{\sinh^{-1} \left\{ \frac{2 + \rho_a}{2\kappa_a(1 - 2\varphi_a)} \right\} - \sinh^{-1} \left\{ \frac{1 + \rho_a}{2\kappa_a(1 - \varphi_a)} \right\}}{\sinh^{-1} \left\{ \frac{2 - \rho_a}{2\kappa_a(1 + 2\varphi_a)} \right\} - \sinh^{-1} \left\{ \frac{1 - \rho_a}{2\kappa_a(1 + \varphi_a)} \right\}} \end{aligned} \right\} \quad (22a)$$

Substitution of (21b) in (18b) gives the equations

$$\left. \begin{aligned} r_1 &= \frac{\sinh^{-1} \left\{ \frac{1 + \varrho_b}{2\kappa_b(1 + \varphi_b)} \right\} - \sinh^{-1} \left\{ \frac{\varrho_b}{2\kappa_b} \right\}}{\sinh^{-1} \left\{ \frac{1 - \varrho_b}{2\kappa_b(1 - \varphi_b)} \right\} + \sinh^{-1} \left\{ \frac{\varrho_b}{2\kappa_b} \right\}} \\ r_2 &= \frac{\sinh^{-1} \left\{ \frac{2 - \varrho_b}{2\kappa_b(1 - 2\varphi_b)} \right\} - \sinh^{-1} \left\{ \frac{1 - \varrho_b}{2\kappa_b(1 - \varphi_b)} \right\}}{\sinh^{-1} \left\{ \frac{1 + \varrho_b}{2\kappa_b(1 + \varphi_b)} \right\} - \sinh^{-1} \left\{ \frac{\varrho_b}{2\kappa_b} \right\}} \\ r_3 &= \frac{\sinh^{-1} \left\{ \frac{2 + \varrho_b}{2\kappa_b(1 + 2\varphi_b)} \right\} - \sinh^{-1} \left\{ \frac{1 + \varrho_b}{2\kappa_b(1 + \varphi_b)} \right\}}{\sinh^{-1} \left\{ \frac{2 - \varrho_b}{2\kappa_b(1 - 2\varphi_b)} \right\} - \sinh^{-1} \left\{ \frac{1 - \varrho_b}{2\kappa_b(1 - \varphi_b)} \right\}} \end{aligned} \right\} \quad (22)$$

With $\varphi_a \approx 0$ and $\varphi_b \approx 0$, eqns. (22a) and (22b) both yield:

$$\left. \begin{aligned} r_1 &= \frac{\sinh^{-1} \left(\frac{1 + \varrho}{2\kappa} \right) - \sinh^{-1} \left(\frac{\varrho}{2\kappa} \right)}{\sinh^{-1} \left(\frac{1 - \varrho}{2\kappa} \right) + \sinh^{-1} \left(\frac{\varrho}{2\kappa} \right)} \\ r_2 &= \frac{\sinh^{-1} \left(\frac{2 - \varrho}{2\kappa} \right) - \sinh^{-1} \left(\frac{1 - \varrho}{2\kappa} \right)}{\sinh^{-1} \left(\frac{1 + \varrho}{2\kappa} \right) - \sinh^{-1} \left(\frac{\varrho}{2\kappa} \right)} \\ r_3 &= \frac{\sinh^{-1} \left(\frac{2 + \varrho}{2\kappa} \right) - \sinh^{-1} \left(\frac{1 + \varrho}{2\kappa} \right)}{\sinh^{-1} \left(\frac{2 - \varrho}{2\kappa} \right) - \sinh^{-1} \left(\frac{1 - \varrho}{2\kappa} \right)} \end{aligned} \right\}$$

where $\varrho = \varrho_a = \varrho_b$ and $\kappa = \kappa_a = \kappa_b$. Further we define:

$$\kappa = \frac{\sqrt{K}}{t\varphi} \quad \text{and} \quad \varphi = \frac{\Delta v}{V_c}$$

where V_c is the volume of the solution corresponding to the potential between τ_0 and τ . Values of r_1 , r_2 and r_3 have been calculated after substitution of a number of ϱ - and κ -values in the eqns. (23). The results are represented in Fig. 2. Here the ratios r_1 , r_2 and r_3 are plotted against the ratio r_2 and curves are drawn through points referring to equal ϱ - and equal κ -values respectively. When r_2 and r_1 or r_3 are known the ϱ - and κ -value of a symmetric potentiometric titration can be read from Fig. 2. (More details are given in Fig. 7.) Fig. 2 shows that low κ -values (e.g. $\kappa < 0.15$) found from r_1 and r_3 are more accurate than those found from r_2 . Therefore we recommend the determination of the κ -values from r_1 and r_3 .

Effect of dilution

Effect of $\varphi \neq 0$ on ϱ . When $\varphi \neq 0$, eqns. (22a) and (22b) must be used. After substitution of $\varphi = 0.01$ and different values of ϱ_a , κ_a , ϱ_b and κ_b , the ratios r_1 , r_2 and r_3 have been calculated by means of these formulae. The results are represented in Fig. 3

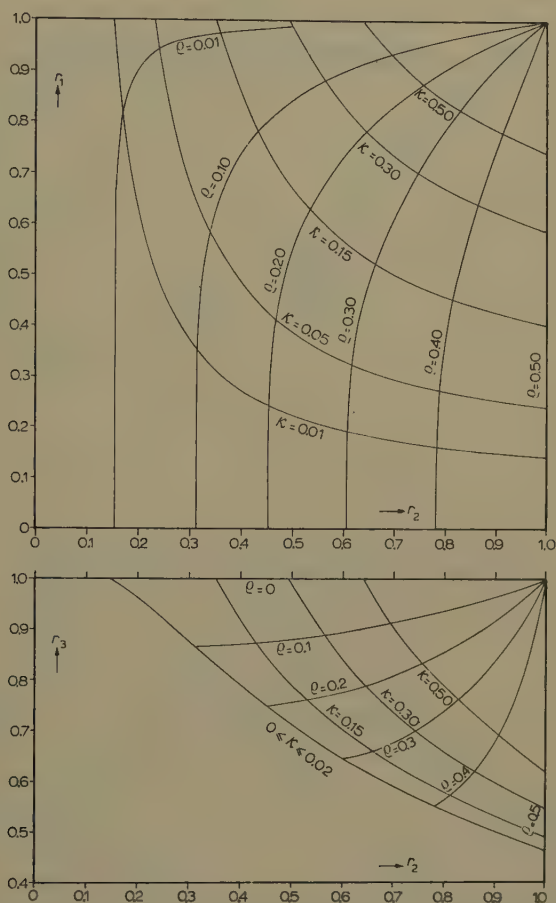


Fig. 3. Each curve referring to constant ϱ - or κ -values ($\varphi = 0$) indicates the relationship between the ratios r_2 and r_1 or r_3 . The data have been calculated with eqn. (23).

The lines are drawn through points referring to equal ϱ_a - and ϱ_b -values. The ϱ_a - and ϱ_b -curves correspond to values calculated with eqns. (22a) and (22b) respectively. The dashed ϱ -curves obtained from the eqns. (23), refer to $\varphi = 0$ and correspond to the ϱ -curves in Fig. 2. Fig. 3 shows that the ϱ -values derived from r_2 and r_3 are more influenced by $\varphi \neq 0$ than the ϱ -values derived from r_1 and r_2 . A deviation $\Delta\varrho \leq 0.015$ (≤ 0.025) of the ϱ -value derived from r_1 and r_2 (r_2 and r_3) can be expected if $\kappa \leq 0.3$ and the influence of $\varphi \leq 0.01$ is neglected. Generally, the value $\Delta\varrho \leq 0.015$ is small in proportion to the deviation in ϱ caused by errors in the experimentally determined ratios of potential steps. Therefore we recommend the determination of ϱ -values from r_1 and r_2 and the neglect of the effect of $\varphi \leq 0.01$ if $\kappa \leq 0.3$.

Effect of $\varphi \neq 0$ on κ . After substitution of $\varphi = 0.01$ and different values of κ_a , ϱ_b and κ_b in eqns. (22a) and (22b), the ratios r_1 , r_2 and r_3 have been calculated. The results are represented in Fig. 4, where lines are drawn through points referring to equal κ_a and κ_b values. The curves marked κ_a and κ_b correspond

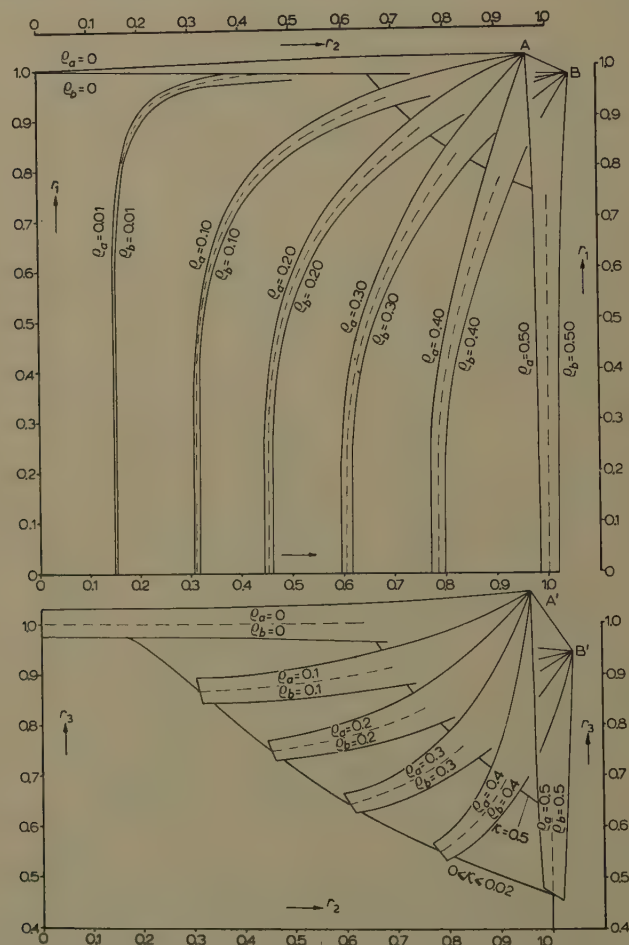


Fig. 3. The full lines ($\varphi_a = 0.01 = \varphi_b$) refer to eqns. (22a) and (22b); the dashed curves ($\varphi_a = 0.01, \varphi_b = 0.01$) refer to the eqns. (23).

values found from eqns. (22a) and (22b) respectively. Each κ -curve represents Fig. 2 and referring to $\varphi = 0$, lies between the corresponding κ_a - and κ_b -curves in Fig. 4. Fig. 4 shows that the influence of $\varphi \neq 0$ on the κ -values derived from r_1 and r_2 is smaller than the effect of $\varphi \neq 0$ on the κ -values from r_3 . Consequently, if the influence of $\varphi \neq 0$ is neglected κ -values derived from r_1 and r_2 are to be preferred. In the next section it will be shown that if $\kappa \leq 0.5$ and the influence of $\varphi \leq 0.01$ is neglected the errors in the ratios of the potential steps found from experimental data determine the accuracy of κ .

Introduction of potential steps of decreasing order. If a solution is titrated with e

elements Δv of the reagent and Δ_0 , Δ_1 and Δ_2 are potential steps of decreasing order, ratios:

$$R_1 = \frac{\Delta_1}{\Delta_0} \quad \text{and} \quad R_2 = \frac{\Delta_2}{\Delta_1}$$

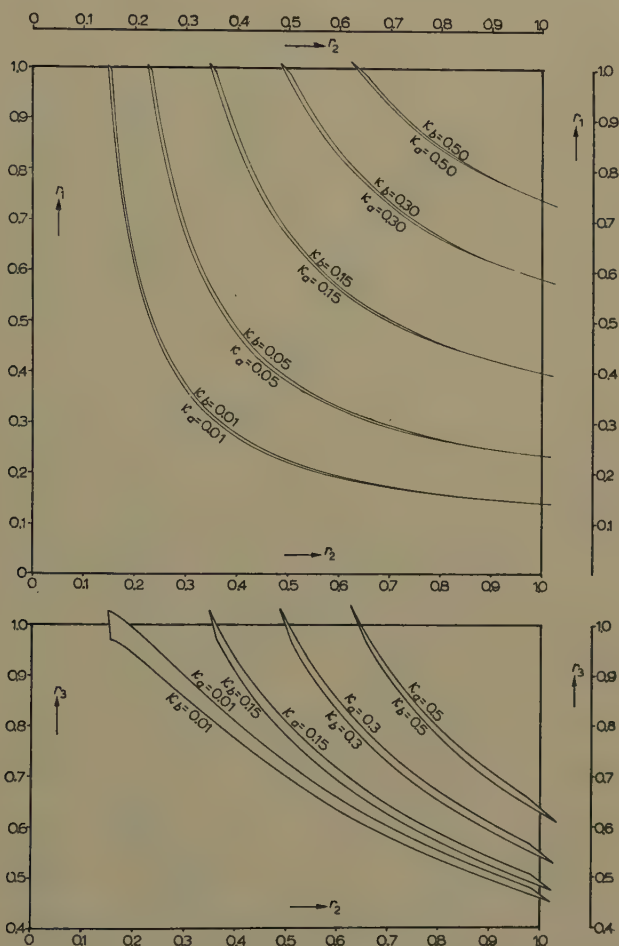


Fig. 4. The curves refer to data calculated with eqns. (22a) and (22b) after substitution of $\varphi_a = 0.01 = \varphi_b$.

not exceed the value 1. From Fig. 1 it can be seen that generally:

$$R_1 = \frac{\Delta_1}{\Delta_0} = \frac{\tau_1}{\tau_0} = r_1 \quad \text{and} \quad R_2 = \frac{\Delta_2}{\Delta_1} = \frac{\tau_2}{\tau_1} = r_2 \quad (24)$$

however, $\varphi \neq 0$ the ratios r_1 and r_2 may occasionally exceed the value 1. With $r_1 > 1$ (see points near $\varphi_a = 0$ in Fig. 3) and $r_2 > 1$ (see points near $\varphi_b = 0.5$ in Fig. 3) the eqns. (24) are not applicable. With $r_1 > 1$ (see Fig. 5a) it appears that:

$$R_1 = \frac{\Delta_1}{\Delta_0} = \frac{\tau_0}{\tau_1} = \frac{1}{r_1} \quad \text{and} \quad R_2 = \frac{\Delta_2}{\Delta_1} = \frac{\tau_3}{\tau_0} = r_1 r_2 r_3 \quad (25a)$$

With $r_2 > 1$ (see Fig. 5b) we get:

$$R_1 = \frac{\Delta_1}{\Delta_0} = \frac{\tau_2}{\tau_0} = r_1 r_2 \quad \text{and} \quad R_2 = \frac{\Delta_2}{\Delta_1} = \frac{\tau_1}{\tau_2} = \frac{1}{r_2} \quad (2)$$

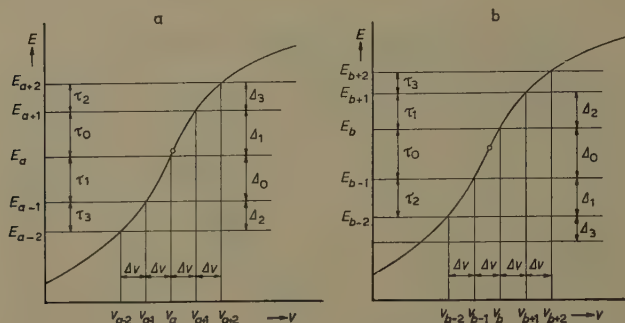


Fig. 5. Potential volume curves (effect of dilution not neglected).

After substitution of $\varphi_a = 0.05 = \varphi_b$ and different values of q_a , κ_a , q_b and κ_b in the eqns. (22) we calculated the ratios r_1 , r_2 and r_3 . Substitution of the results in eqns. (24) and (25) leads to the R_1 - and R_2 -values plotted in Fig. 6. In this figure curves have been drawn through points with equal κ_a - and κ_b -values. The dashed κ -lines which refer to $\varphi = 0$, have been obtained by the eqns. (23) and correspond to κ -lines in Fig. 2.

If the effect of $\varphi \leq 0.05$ is neglected, each pair of full lines shows the maximum deviations of the κ -values from the corresponding dashed curves. Fig. 6 shows that these deviations are smaller than the deviations caused by errors in the experimentally determined ratios R_1 and R_2 (the errors in R_1 and R_2 do not exceed 5% if

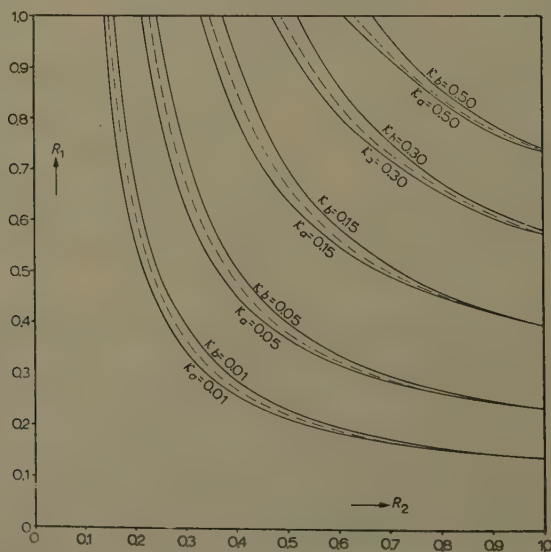


Fig. 6. The full lines ($\varphi_a = 0.05 = \varphi_b$) refer to data calculated with (22), (24) and (25); the dashed lines ($\varphi = 0$) to data derived from eqns. (23) and (24).

experimental conditions are favourable). Consequently, the effect of $\varphi \leq 0.05$ on κ may be neglected if $\kappa \leq 0.5$.

PROCEDURE

The method can be applied to potentiometric titrations of the type:



The procedure can be summarized as follows:

- a) Take V ml of the solution containing the substance A.
- b) Titrate with equal portions Δv ($\leq 0.01 V$) of D, titre t .
- c) Determine the potential steps in decreasing order Δ_0 , Δ_1 and Δ_2 and the added volume v_e , which corresponds with the potential between Δ_0 and Δ_1 .
- d) Calculate the ratios

$$R_1 = \Delta_1/\Delta_0, R_2 = \Delta_2/\Delta_1 \text{ and } \varphi = \Delta v/(V + v_e). \quad (26)$$

- e) Determine the parameters ϱ and κ from R_1 , R_2 and Fig. 7.

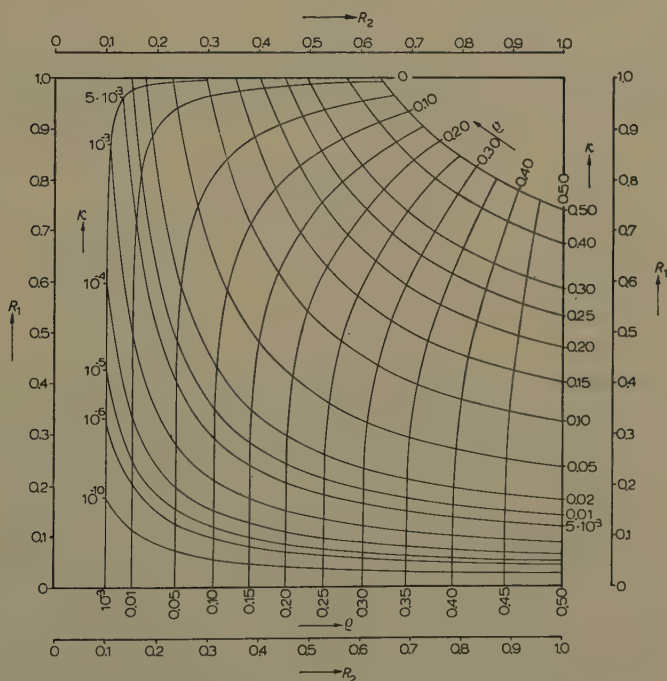


Fig. 7. Nomograph for reading ϱ - and κ -values (effect of dilution neglected).

- f) Calculate the equivalence amount v_0 from:

$$\begin{aligned} v_0 &= v_e + \varrho \Delta v \quad (27a) \text{ if } \Delta_1 \text{ precedes } \Delta_0; \text{ or} \\ v_0 &= v_e - \varrho \Delta v \quad (27b) \text{ if } \Delta_0 \text{ precedes } \Delta_1. \end{aligned} \quad (27)$$

With $\varphi \leq 0.01$ and $\kappa \leq 0.3$ the accuracy of ϱ is determined by the errors in R_1 and R_2 .

(g) Calculate the ionization constant from:

$$K = (t\varphi\kappa)^2 \quad (28)$$

With $\varphi \leq 0.05$ and $\kappa \leq 0.5$ the accuracy of κ is determined by the errors in R_1 and R_2 .

(f) The limits of the applicability of the method are:

$$\frac{\sqrt{K}}{t} \leq 3 \cdot 10^{-3} \text{ if } \varrho \text{ is to be determined, and} \quad (29a)$$

$$\frac{\sqrt{K}}{t} \leq 25 \cdot 10^{-3} \text{ if } \kappa \text{ is to be determined.} \quad (29b)$$

DISCUSSION OF VARIOUS CALCULATION METHODS

Procedures

The procedures of two other methods will be summarized. They are applied after potentiometric titration of a solution carried out by addition of constant increments Δv of the reagent.

(a) KOLTHOFF¹⁻³ recommends determination of the largest potential step Δ_0 , step Δ_b and Δ_a before and after Δ_0 respectively and the volume v_K , which correspond with the potential between Δ_b and Δ_0 . After calculation of the parameter:

$$\varrho_K = \frac{\Delta_0 - \Delta_b}{2 \Delta_0 - (\Delta_a + \Delta_b)} \quad (30)$$

the equivalence amount v_0 is derived from

$$v_0 = v_K + \varrho_K \Delta v \quad (31)$$

(b) HAHN⁹ determines the potential steps in decreasing order Δ_0 , Δ_1 , Δ_2 and the volume v_c , which corresponds to the potential between Δ_0 and Δ_1 . After calculation of $R_1 = \Delta_1/\Delta_0$, $R_2 = \Delta_2/\Delta_1$ and $R_3 = \Delta_3/\Delta_2$ the parameter ϱ_H is found from:

$$\left. \begin{array}{lll} (i) \quad \varrho_H = \frac{1}{2} R_2 & \text{if } R_1 \leq \frac{1}{2} R_2 & \text{and } 0.30 \leq \frac{1}{2} R_2 \leq 0.50 \\ (ii) \quad \varrho_H = \frac{1}{2} R_2 - 0.35(0.3 - \frac{1}{2} R_2) & \text{if } R_1 \leq \frac{1}{2} R_2 & \text{and } 0.15 < \frac{1}{2} R_2 < 0.30 \\ (iii) \quad \varrho_H = -1.58 \log R_3 & \text{if } R_1 \leq \frac{1}{2} R_2 & \text{and } 0 \leq \frac{1}{2} R_2 \leq 0.15 \\ & \text{or if } R_1 > \frac{1}{2} R_2 \end{array} \right\} \quad (32)$$

The equivalence amount v_0 is calculated from:

$$\begin{aligned} v_0 &= v_c + \varrho_H \Delta v, \text{ if } \Delta_1 \text{ precedes } \Delta_0 \\ \text{or } v_0 &= v_c - \varrho_H \Delta v, \text{ if } \Delta_0 \text{ precedes } \Delta_1 \end{aligned} \quad (33)$$

(c) The ϱ -value found by our method will be indicated with the symbol ϱ_F . In the next section the values of ϱ_K , ϱ_H and ϱ_F will be compared to the neglect of the effect of dilution.

Comparison of the methods

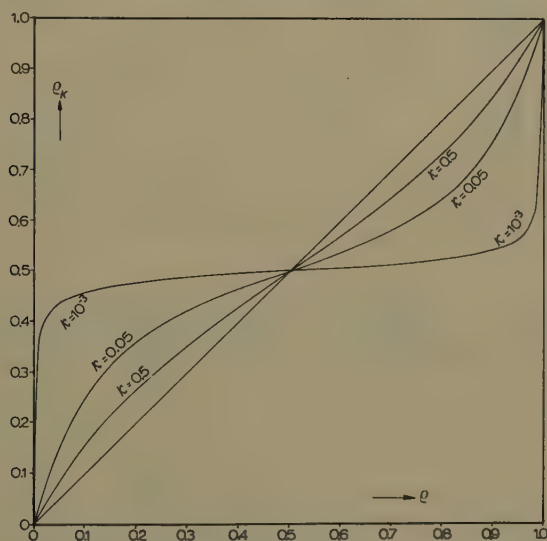
If $\Delta_b > \Delta_a$, we obtain $\Delta_b = \Delta_1$ and $\Delta_a = \Delta_2$. Substitution of these data and eqn. (30) gives

$$\varrho_K = 0.5 - \frac{0.5 R_1(1 - R_2)}{2 - R_1(1 + R_2)} \quad (34a)$$

If $\Delta_b < \Delta_a$, we obtain $\Delta_b = \Delta_2$ and $\Delta_a = \Delta_1$. Substitution of these data and eqn. (24) and (30) gives

$$\varrho_K = 0.5 + \frac{0.5 R_1(1 - R_2)}{2 - R_1(1 + R_2)} \quad (34b)$$

After substitution of different ϱ - and κ -values in the eqns. (23), the ratios $R_1 (= r_1)$, $R_2 (= r_2)$ and $R_3 (= r_3)$ have been calculated. Substitution of these ratios in eqns. (32) and (34) and application of the procedures described above, give the values of ϱ_K , and ϱ_F . These data have been plotted against the true ϱ -value in Figs. 8 and 9.



8. Comparison between the ϱ_K -values found by Kolthoff's method and the true ϱ -values (effect of dilution neglected).

Fig. 8 shows that large deviations occur between ϱ_K and ϱ . These deviations increase with increasing κ -values. With $\kappa < 10^{-3}$, $\varrho_K \approx 0.5$ is found for nearly all ϱ -values. As a result, systematic errors will be introduced when the equivalence point is determined by interpolation with ϱ_K -values. Fig. 9 shows that the deviations between ϱ_K and ϱ decrease with decreasing κ -values; ϱ_K and ϱ are equal when $0 < \kappa < 0.10$. We have already pointed out that ϱ_F and ϱ are equal at all κ -values.

Influence of κ on the potential-volume curve

If the effect of dilution is neglected ($\varphi_a = 0$) and $Z_{a+n} = Z$ eqn. (21a) leads to:

$$Z = \sinh^{-1} \left(\frac{n - \varrho}{2\kappa} \right) \quad (35)$$

In Fig. 10 the values of Z (proportional to the potential E) obtained from eqn. (35) have been plotted against n (proportional to the volume v). The influence of κ on the type of the titration curve becomes clear from Fig. 10.

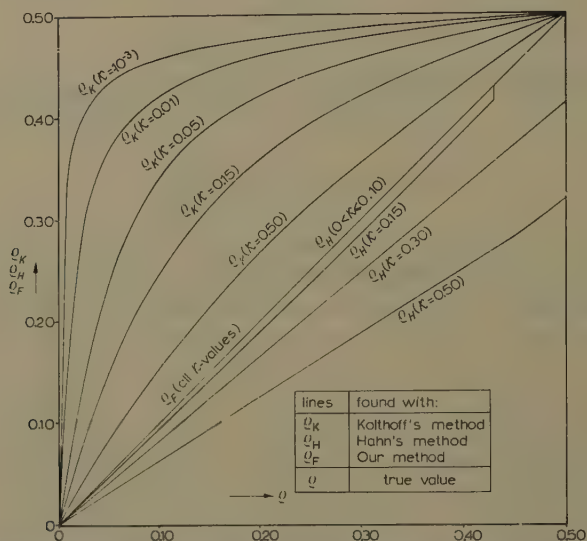


Fig. 9. Comparison between the ρ -values found by Kolthoff's, Hahn's and our method and the true ρ -values (effect of dilution neglected). ρ_K , lines found by Kolthoff's method; ρ_H , lines found by Hahn's method; ρ_F , lines found by our method; ρ , true value.

The dots on each curve correspond to equidistant volumes and to the four potentials — two before and two after the equivalence point — needed for determining the end-point and the ionization constant by our method.

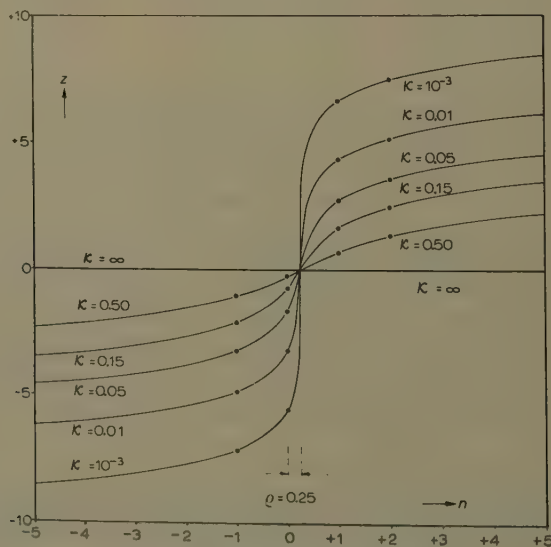


Fig. 10. Symmetric titration curve with different κ -values (effect of dilution neglected). The lines refer to data found with eqn. (35).

Table I shows the ϱ -values found by application of the three methods to the data corresponding to the dots in Fig. 10. These data, which can also be read from Fig. 9, confirm the conclusions of the foregoing section.

TABLE I

x	True value ϱ	Found		
		ϱ_K	ϱ_H	ϱ_F
10^{-3}	0.25	0.48	0.25	0.25
0.01	0.25	0.47	0.25	0.25
0.05	0.25	0.44	0.25	0.25
0.15	0.25	0.39	0.24	0.25
0.50	0.25	0.31	0.16	0.25

TABLE II TITRATION OF 45 ml KIO_3 (0.1 N HNO_3) WITH 0.100 N AgNO_3

Found			Calculated	
v ml	E mV	Δ mV	v_0 ml	K mequiv./ml ²
3.80	292	Δ_1	$R_1 = 0.615$	$n = 0.100$
4.30	308		$R_2 = 0.875$	$\Delta v = 0.50$
4.80	332		$\varrho = 0.42$	$V = 45$
5.30	371		$v_c = 4.80$	$\varphi = 1.00 \cdot 10^{-2}$
5.80	392		$v_0 = 5.01$	$x = 0.28$
6.30	404	Δ_2		$K = 8 \cdot 10^{-8}$

Conclusion

If in a symmetric potentiometric titration the reagent is added in equal volumes, the end-point lies between the volumes corresponding to the boundaries of the maximum potential step. Consequently, if Δv is very small in proportion to the total amount of reagent added at the end-point, the equivalence point can be accurately determined without any interpolation being required. We can then agree with KOLTHOFF's statement³, concerning the method of HAHN *et al.*¹³: "their methods do not give more information than we obtain from much simpler procedures".

If, however, an interpolation is required, we must agree with HAHN's view⁸ that KOLTHOFF's method leads to inaccurate results*.

TABLE III TITRATION OF 50 ml NaCl WITH 0.100 N AgNO_3

Found			Calculated	
v ml	E a.u. ^a	Δ a.u.	v_0 ml	K mequiv./ml ²
1.50	7.59	Δ_2	$R_1 = 0.179$	$n = 0.100$
2.00	7.37		$R_2 = 0.732$	$\Delta v = 0.50$
2.50	6.96		$\varrho = 0.38$	$V = 50$
3.00	3.84		$v_c = 3.00$	$\varphi = 0.94 \cdot 10^{-2}$
3.50	3.28		$v_0 = 2.81$	$x = 0.012$
4.00	3.07	Δ_1		$K = 1.3 \cdot 10^{-10}$

* a.u. = arbitrary units (proportional to the potential in mV)

The author hopes that his paper may contribute towards making peace in "the thirty years' war" about this subject between F. L. HAHN and I. M. KOLTHOFF.

EXPERIMENTAL

In order to check our method we have performed a number of potentiometric titrations. About 50 ml of each solution were carefully titrated by addition of constant increments Δv of 0.1 N reagent from a piston burette at 25° with constant stirring. The experimental data and the values derived by our method are represented in Tables II–VII.

TABLE IV TITRATION OF 50 ml KCNS WITH 0.100 N AgNO_3

Found			Calculated		
<i>v</i> ml	<i>E</i> a.u.	Δ a.u.	<i>v</i> ₀ ml	<i>K</i> mequiv. ² /ml ²	
1.50	7.38	$\left. \begin{array}{l} 7 \\ 15 \\ 150 \\ 16 \\ 6 \end{array} \right\} \begin{array}{l} \Delta_2 \\ \Delta_0 \\ \Delta_1 \end{array}$	$R_1 = 0.107$	$n = 0.100$	
2.00	7.31		$R_2 = 0.94$	$\Delta v = 0.50$	
2.50	7.16		$\varrho = 0.48$	$V = 50$	
3.00	5.66		$v_c = 3.00$	$\varphi = 0.94 \cdot 10^{-2}$	
3.50	5.50		$v_0 = 2.76$	$\kappa = 2 \cdot 10^{-3}$	
4.00	5.44			$K = 3.5 \cdot 10^{-12}$	

TABLE V TITRATION OF 50 ml HCl (IN 0.1 N NaCl) WITH 0.1000 N NaOH

Found			Calculated		
<i>v</i> ml	pH	Δ a.u.	<i>v</i> ₀ ml	<i>K</i> mequiv. ² /ml ²	
(a)					
1.50	3.12	$\left. \begin{array}{l} 17 \\ 32 \\ 628 \\ 109 \\ 22 \end{array} \right\} \begin{array}{l} \Delta_2 \\ \Delta_0 \\ \Delta_1 \end{array}$	<i>R</i> ₁ = 0.174	<i>n</i> = 0.100	
2.00	3.29		<i>R</i> ₂ = 0.294	Δv = 0.50	
2.50	3.61		<i>Q</i> = 0.09	<i>V</i> = 50	
3.00	9.89		<i>v</i> _c = 3.00	φ = 0.94 · 10 ⁻²	
3.50	10.98		<i>v</i> ₀ = 2.96	κ = 2 · 10 ⁻⁴	
4.00	11.20			<i>K</i> = 3.5 · 10 ⁻¹⁴	
(b)					
1.50	3.16	$\left. \begin{array}{l} 17 \\ 29 \\ 638 \\ 100 \\ 25 \end{array} \right\} \begin{array}{l} \Delta_2 \\ \Delta_0 \\ \Delta_1 \end{array}$	<i>R</i> ₁ = 0.157	<i>n</i> = 0.1000	
2.00	3.33		<i>R</i> ₂ = 0.290	Δv = 0.50	
2.50	3.62		<i>Q</i> = 0.08	<i>V</i> = 50	
3.00	10.00		<i>v</i> _c = 3.00	φ = 0.94 · 10 ⁻²	
3.50	11.00		<i>v</i> ₀ = 2.96	κ = 1.0 · 10 ⁻⁴	
4.00	11.25			<i>K</i> = 0.9 · 10 ⁻¹⁴	

TABLE VI TITRATION OF 50 ml NaI WITH 0.100 N AgNO_3

Found			Calculated		
<i>v</i> ml	<i>E</i> a.u.	Δ a.u.	<i>v</i> ₀ ml	<i>K</i> mequiv. ² /ml ²	
(a)					
1.50	7.78	$\left. \begin{array}{l} 9 \\ 59 \\ 260 \\ 9 \\ 5 \end{array} \right\} \begin{array}{l} \Delta_1 \\ \Delta_0 \\ \Delta_2 \end{array}$	<i>R</i> ₁ = 0.227	<i>n</i> = 0.100	
2.00	7.69		<i>R</i> ₂ = 0.153	Δv = 0.50	
2.50	7.10		<i>ρ</i> = 0.01	<i>V</i> = 50	
3.00	4.50		<i>v</i> _c = 2.50	<i>φ</i> = 0.95 · 10 ⁻²	
3.50	4.41		<i>v</i> ₀ = 2.50	<i>κ</i> = 5 · 10 ⁻⁸	
4.00	4.36			<i>K</i> = 0.23 · 10 ⁻¹⁶	
(b)					
1.50	7.78	$\left. \begin{array}{l} 10 \\ 80 \\ 238 \\ 9 \\ 5 \end{array} \right\} \begin{array}{l} \Delta_1 \\ \Delta_0 \\ \Delta_2 \end{array}$	<i>R</i> ₁ = 0.336	<i>n</i> = 0.100	
2.00	7.68		<i>R</i> ₂ = 0.113	Δv = 0.50	
2.50	6.88		<i>ρ</i> = 0.002	<i>V</i> = 50	
3.00	4.50		<i>v</i> _c = 2.50	<i>φ</i> = 0.95 · 10 ⁻²	
3.50	4.41		<i>v</i> ₀ = 2.50	<i>κ</i> = 7 · 10 ⁻⁶	
4.00	4.36			<i>K</i> = 0.44 · 10 ⁻¹⁶	

TABLE VII IONIZATION CONSTANTS AT 25°C

Substance	See Table	K value		pK value	
		Calculated	Literature ^a	Calculated	Literature
AgIO ₃	II	8·10 ⁻⁸	3·10 ⁻⁸	7.1	7.5
AgCl	III	1.3·10 ⁻¹⁰	1.7·10 ⁻¹⁰	9.9	9.8
AgCNS	IV	3.5·10 ⁻¹³	1.0·10 ⁻¹²	11.5	12.0
H ₂ O	V(a)	3.5·10 ⁻¹⁴	1.0·10 ⁻¹⁴	13.5	14.0
	V(b)	0.9·10 ⁻¹⁴	1.0·10 ⁻¹⁴	14.0	14.0
AgI	VI(a)	0.23·10 ⁻¹⁶	0.85·10 ⁻¹⁶	16.6	16.1
	VI(b)	0.44·10 ⁻¹⁶	0.85·10 ⁻¹⁶	16.4	16.1

From the experimental data (Tables II–VII) we may conclude that our method is simple, requires no graphical representation of the measurements and leads to approximate values of the ionization constants.

ACKNOWLEDGEMENT

We wish to thank Mr. J. L. H. SOONS, of the Analytical Department of our Laboratory, who calculated the numerical values plotted in the figures.

SUMMARY

A method is developed for calculating the end-point and the ionization constant in a potentiometric titration. The influence of dilution is studied. The method is compared with the procedure of KOLTHOFF and that of HAHN.

RÉSUMÉ

La méthode a été mise au point pour le calcul du point final et de la constante d'ionisation lors d'un titrage potentiométrique. On étudie l'influence de la dilution. On compare la méthode aux méthodes recommandées par KOLTHOFF et par HAHN.

ZUSAMMENFASSUNG

Es wurde eine Methode zur Berechnung des Endpunktes und der Ionisationskonstante bei einer potentiometrischen Titration entwickelt. Ferner wurde der Einfluss der Verdünnung untersucht. Die Methode wurde sowohl mit dem von KOLTHOFF wie vom HAHN empfohlenen Verfahren verglichen.

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POLAROGRAPHIC ANALYSIS USING POTASSIUM IODIDE AS SUPPORTING ELECTROLYTE*

III. THE POLAROGRAPHIC BEHAVIOR OF TRIVALENT ARSENIC

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INTRODUCTION

Polarographic studies on trivalent arsenic in 1 *M* hydrochloric acid have been reported by several authors¹⁻⁵. KACIRKOVA¹ reported that the reduction wave of arsenious acid in this medium consisted of two steps at approximately -0.3 V and -0.6 V *vs.* SCE. The first wave which resulted from the reduction of arsenious acid to metallic arsenic was not used for quantitative analysis, but the height of the second wave was proportional to the concentration of arsenic acid.

On the other hand, LINGANE² found two steps with starting potentials of -0.4 and -0.9 V *vs.* SCE in 1 *M* hydrochloric acid; the first wave height was proportional to the concentration of arsenious acid in solutions containing 0.01% gelatine as maximum suppressor and the diffusion current constant was 8.6 at 25°. He suggested that this wave was due to the reduction of arsenic(III) to the elementary state rather than to arsine.

After that, MEITES³ reported the polarographic characteristics of arsenious acid in the same medium without a maximum suppressor. The half-wave potential of the first step was -0.428 V *vs.* SCE and the diffusion current constant was 6.04, which is smaller than the value reported by LINGANE. The wave height of the first step was proportional to the concentration of arsenic in the range between 0.018 and 0.9 mM and the wave height became constant at concentrations higher than 0.9 mM and was independent of changes in temperature, concentration of hydrochloric acid or arsenic.

Since we have studied the polarographic behavior of several metal ions in solutions of potassium iodide as a supporting electrolyte⁶⁻⁷, the usefulness of the method has been recognized for polarographic analysis, particularly as a well-separated reduction wave was given for a sample containing indium and cadmium⁶.

In this paper, the polarographic behavior of trivalent arsenic is described in solutions of 0.1 to 1.0 *M* potassium iodide containing 0 to 0.0015% of dodecyl trimethyl ammonium chloride as a maximum suppressor.

EXPERIMENTAL

All polarograms were recorded by the Yanagimoto pen-recording polarograph, Model

* Parts I and II in this series were presented in the *Repts. Govt. Ind. Research Inst., Nagoya* 8 (1959) 638; 9 (1960) 28.

3-4. The flow rate of mercury, m , and the drop-time were respectively 1.41 mg/sec and 3.41 sec/drop at the applied potential of -0.80 V vs. SCE; the height of mercury column was $h = 68.5$ cm Hg. A saturated calomel electrode was used as a reference electrode and was connected to the solution through an agar bridge.

All experiments were carried out in a thermostat maintained at $25 \pm 0.1^\circ$. The pH value of the solution was measured with a Horiba glass electrode pH-meter, Model 3.

The 0.02 M arsenic stock solution was prepared by dissolving reagent-grade arsenic trioxide in a minimal volume of 2 N potassium hydroxide followed by acidification with hydrochloric acid and dilution to a known volume with distilled water. A 2 M potassium iodide solution was used as supporting electrolyte and was prepared from analytical grade reagent. Solutions of DTAC and other surface active substances used as maximum suppressors were 0.01%.

The electrolytic sample solutions were prepared by the following procedure. To a certain volume of the stock solution of arsenic, sufficient supporting electrolyte and maximum suppressor were added to reach the final concentrations: 0.1 M to 1.0 M KI and 0.0005% to 0.0015%, respectively. The pH value of the sample solution was then adjusted by adding a little dilute hydrochloric acid or potassium hydroxide.

Dissolved oxygen was removed by bubbling pure nitrogen gas through the sample solution for about 15 min. Then the polarograms were recorded.

RESULTS AND DISCUSSION

The reduction waves of trivalent arsenic in 0.1 M potassium iodide containing DTAC and the maximum suppressor are shown in Fig. 1. The first step was a well-defined wave

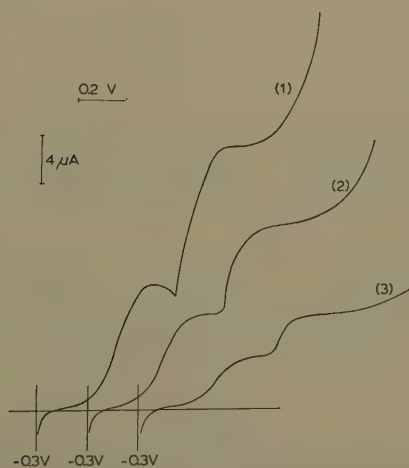


Fig. 1. The reduction waves of arsenic(III) in 0.1 M KI. (1) 1.2 mM As^{+3} , 0.001% DTAC; (2) 0.8 mM As^{+3} , 0.001% DTAC; (3) 0.4 mM As^{+3} , 0.001% DTAC.

at concentrations of arsenic less than 0.8 mM (Curves 2 and 3), but the wave did not show a plateau pattern at concentrations of trivalent arsenic higher than 1.0 mM . The reduction current rose slowly and fell with increasing applied potential, *i.e.* the wave developed a roundish pattern (Curve 1).

The second wave, in the absence of a maximum suppressor, had a curious double maximum wave which could not be suppressed by gelatine (Fig. 2, Curve 1); several surface-active substances were tested as maximum suppressors and DTAC was found to be the most useful. The effects of DTAC on the reduction wave of trivalent arsenic in 0.1 *M* potassium iodide are shown in Fig. 2. The same characteristics as in the first wave are indicated.

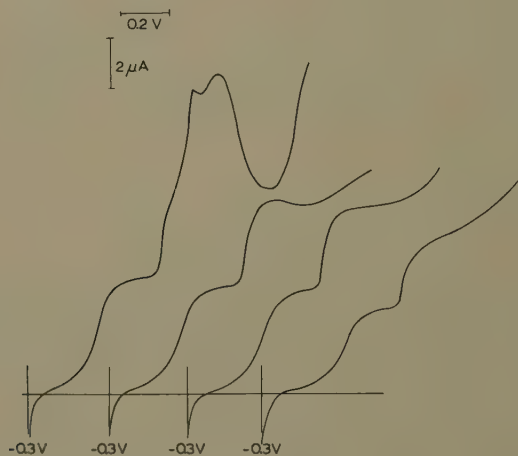


Fig. 2. The effect of DTAC on the reduction waves: As^{+3} , 0.4 mM; KI, 0.1 *M*; pH = 2.1 to 2.4. (1) DTAC 0; (2) DTAC 0.0005%; (3) DTAC 0.0010%; (4) DTAC 0.0015%.

Influence of the effective pressure on the dropping mercury electrode and of temperature on the limiting current

When the heights of mercury column were altered, the limiting current of the first wave or the total wave was recorded both in the absence and presence of DTAC. Tables I, II and III show the results. The limiting currents of the first wave in the absence of DTAC and those of the first wave or total wave in the presence of DTAC were proportional to the square root of the effective height on the mercury column (corrected for the back pressure).

The temperature coefficients of the limiting current in the presence and absence of DTAC were found to be 1.4% and 1.7% per $^{\circ}\text{C}$, respectively.

From these results, it is considered that the limiting currents in the case described are diffusion-controlled.

TABLE I

RELATION BETWEEN LIMITING CURRENT AND MERCURY PRESSURE ON THE FIRST WAVE

$h(\text{cm})$	h_{corr}	$i_l (\mu\text{A})$	i_l/h_{corr}
53.5	7.20	3.02	0.420
57.5	7.47	3.08	0.416
61.5	7.79	3.16	0.409
65.5	7.99	3.25	0.409

KI, 0.1 *M*; As^{+3} , 0.4 mM; pH, 2.45.

TABLE II

RELATION BETWEEN LIMITING CURRENT AND MERCURY PRESSURE ON THE FIRST WAVE

$h(\text{cm})$	h_{corr}	$As^{+3} (\text{mM})$	i_l	i_l/h_{corr}
63	7.810	0.8	5.97	0.764
67	8.062	0.8	6.45	0.800
71	8.426	0.8	6.43	0.763
75	8.544	0.8	6.79	0.795
KI, 0.1 M; DTAC, 0.001%; pH, 2.48.				
63	7.810	0.4	2.75	0.353
67	8.062	0.4	2.87	0.356
71	8.426	0.4	3.03	0.359
75	8.544	0.4	3.08	0.360
KI, 0.1 M; DTAC, 0.001%; pH, 2.38.				

TABLE III

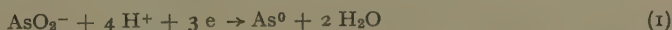
RELATION BETWEEN LIMITING CURRENT AND MERCURY PRESSURE ON THE TOTAL WAVE

$h(\text{cm})$	h_{corr}	$As^{+3} (\text{mM})$	$i_l (\mu A)$	i_l/h_{corr}
63	7.810	0.8	12.77	1.64
67	8.062	0.8	13.17	1.63
71	8.426	0.8	13.53	1.61
75	8.544	0.8	13.95	1.63
KI, 0.1 M; DTAC, 0.001%; pH, 2.48.				
63	7.810	0.4	6.121	0.784
67	8.062	0.4	6.362	0.789
71	8.426	0.4	6.573	0.780
75	8.544	0.4	6.704	0.785
KI, 0.1 M; DTAC, 0.001% pH, 2.48.				

Effects of pH on the reduction wave

The effects of pH on the half-wave potential and the diffusion currents were studied; the characters of the arsenic(III) reduction wave in the pH range 1.90 to 2.76 are shown in Figs. 3 and 4. Below pH 1.9, the starting point of the first wave was so close to the anodic wave of dissolution of mercury that measurements of the wave height were very difficult. The height of the first wave decreased with increasing pH in the range 1.90 to 2.50, but the total wave height showed a constant value (Fig. 3). Above pH 3.00, the wave height apparently decreased with increasing pH. The results indicate that the reduction of trivalent arsenic decreases with a decrease in the concentration of hydrogen ions.

The half-wave potentials of both the first and second waves shifted to more negative values with increasing pH; the second wave shifted farther than the first (Fig. 4). The relationship between the half-wave potential of the first wave and the pH was linear, with the gradient about 115 mV per pH unit. The reduction of arsenious acid at the dropping mercury electrode is considered to proceed as follows:



Therefore, the relationship between the half-wave potential and pH can be written

$$E_{1/2} = E_0 - \frac{0.059}{n} m \text{ pH} + \frac{0.059}{n} \ln \frac{f_R \sqrt{D_0}}{f_O \sqrt{D_R}} \quad (2)$$

where f_R and f_O are the activities of the reductant and oxidant respectively, and D_R and D_O are the corresponding diffusion coefficients. If the reaction proceeds reversibly $n = 3$ and $m = 4$, and the value of $\Delta E_{1/2}$ per pH unit should be 80 mV from eqn. (2). But the value found showed greater shifts than would be expected if the reaction proceeded reversibly.

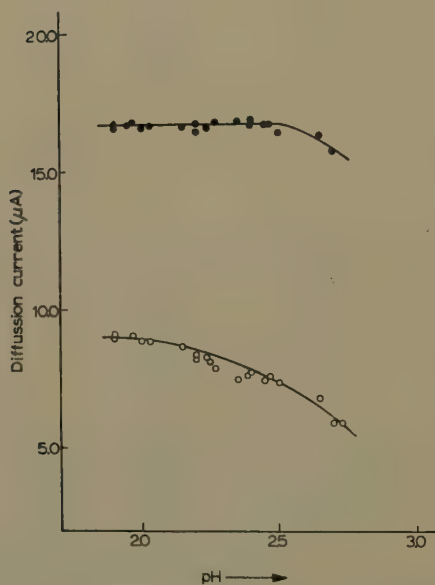


Fig. 3. The effect of pH on the wave height: As^{+3} , 1.0 mM; KI, 0.1 M; pH = 1.9 to 3.5. —●—●— total wave; —○—○— first wave.

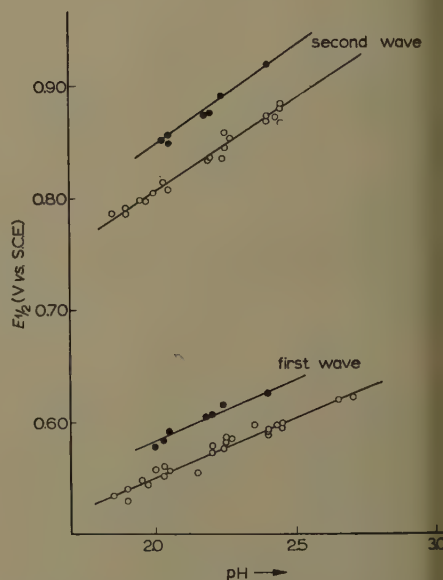


Fig. 4. The effect of pH on the half wave potential: As^{+3} , 1.0 mM; KI, 0.1 M (—●—●—) and 1.0 M (—○—○—); pH = 1.9 to 3.5.

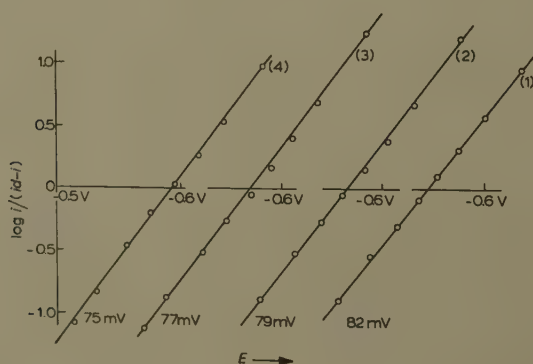
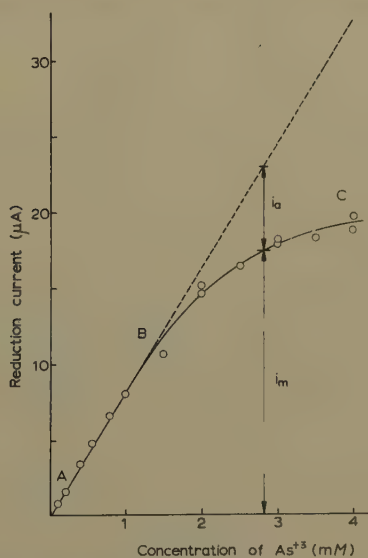


Fig. 5. The plots of $E - \log[i/(i_d - i)]$ of the first wave at several pH values: (1) pH = 2.0, (2) pH = 2.20, (3) pH = 2.25, (4) pH = 2.45. The values shown at the foot of each curve are the reciprocal slopes.

In order to learn more about the nature of the irreversible reduction of trivalent arsenic in potassium iodide solution, the reduction wave was analysed by a logarithmic method. As shown in Fig. 5, the plots of $E - \log i/(i_a - i)$ of the first wave showed a linear dependence at pH values of 2.00, 2.20, 2.25 and 2.45; the gradients are indicated in Fig. 5. Therefore, one can conclude that the reaction $\text{As}^{+3} \rightarrow \text{As}^0$ is irreversible, because the reciprocal slope of the first wave showed a value greater than the theoretical (three electrons). The reciprocal slope of the first wave at a certain pH is not a constant, the value decreasing with increasing pH. It is evident that the irreversible reduction of trivalent arsenic is dependent on the pH of the solution.

Relation between the reduction current and trivalent arsenic concentration

When concentrations varying from 0.06 mM to 4.00 mM of arsenious acid were adjusted to pH 2.0 to 2.4, and the reduction waves were recorded, the height of the first reduction wave increased proportionally to the concentration of arsenic only in the range from 0.06 mM to 0.8 mM (Fig. 6, A and B); however, above 1.0 mM of



6. Relation between the reduction current and the concentration of As^{+3} in 0.1 M KI. The broken line shows the value extrapolated from the linear at low concentrations.

arsenic the relation between the reduction wave height and the concentration was linear (Fig. 6, B and C), and the diffusion current constant decreased with increasing concentrations of arsenious acid. The reproducibilities of the reduction current were not good in the range 1.0 mM to 2.5 mM of arsenious acid, but were better at higher concentrations.

It is interesting that the point B at which the concentration began to show non-linearity (in Fig. 6) agreed with the point at which the plateau of the first wave changed to a roundish curve (Fig. 1, Curve 1). In an explanation suggested by MEITES³,

it is considered that a film of elemental arsenic adsorbed on the surface of the mercury drop limits the regular diffusion of trivalent arsenic. This adsorption phenomenon was confirmed from the relationship of the concentration and wave height. The difference between the observed current at non-linear relationships and the current extrapolated to a linear relationship between wave height and concentration of arsenic is considered as an adsorption phenomenon. From a general equation of isotherm adsorption, the following equation can be written

$$i_c - i_m = i_a = aC^{1/n}$$

Therefore,

$$\log i_a = \log a + \frac{1}{n} \log C$$

where i_c is the current extrapolated to a linear relation, i_m is the observed current height at non-linear relation, i_a is the difference of these two currents (in Fig. 6), and C is the concentration of arsenic. The plots of $\log i_a$ against $\log C$ show a linear relationship (Fig. 7), consequently a non-linear relationship between the reduction wave

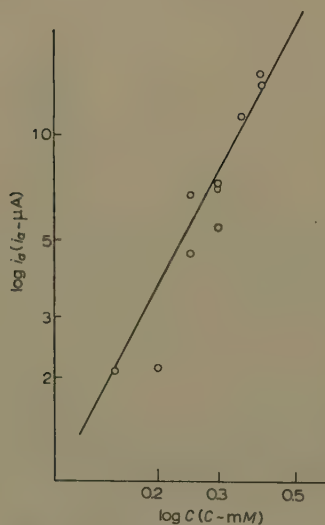


Fig. 7. The adsorption effect of the arsenic concentration on the reduction current.

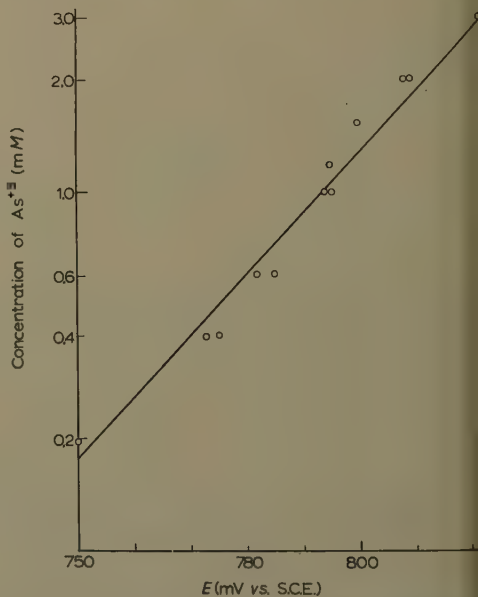


Fig. 8. The effect of the arsenic concentration on the starting potential of the second reduction wave.

height and the concentration can be considered as some effect of an adsorption phenomenon upon the reduction process of arsenic at the surface of the mercury drop.

The reduction current under the conditions of the adsorption phenomenon forms a round pattern with increasing negative potential; the second reduction current appeared suddenly at the end of the drop in the roundish pattern. The curvature of the rounded wave increased with increasing concentrations of arsenious acid, and

The starting potential of the second reduction wave also shifted to negative potentials with increasing concentrations of arsenious acid. The results are given in Fig. 8. The phenomenon is considered as follows. The amount of arsenic adsorbed on the surface of mercury drop increases with shifting negative potentials and the reduction current decreases. At the potential corresponding to the active energy for reduction of the second wave, a sharp reduction current appears. The phenomenon is found to be linearly with increasing concentrations of arsenic; it is considered that the starting potentials of the second wave become more negative, increasing active energy being necessary for reduction of the second wave.

The relationship between the total wave height (the first and second wave heights) and the concentration of arsenious acid is shown in Table IV; the relationship below

TABLE IV

RELATION BETWEEN THE TOTAL WAVE HEIGHT AND THE CONCENTRATION OF ARSENIC

As^{+3} (mM)	i_a (μA)	i_a/C	I
0.06	0.957	15.95	10.33
0.10	1.601	16.01	10.33
0.20	3.271	16.35	10.59
0.40	6.593	16.48	10.68
0.60	9.735	16.23	10.51
0.80	12.98	16.23	10.51
1.00	16.63	16.63	10.77
2.00	33.58	16.78	10.87
3.00	51.11	17.03	11.03
4.00	67.04	16.79	10.86
Mean		16.45 ± 0.36	10.65 ± 0.23

KI, 0.1 M; DTAC, 0.001%; pH, 2.1 to 2.3; $m^{2/3} t^{1/6}$, 1.543.

The concentration 4.0 mM is linear and the total wave height at constant concentration is a constant value over the pH range 1.9 to 2.5. Therefore, the polarographic determination of micro amounts of arsenic in potassium iodide solution seems to be possible.

SUMMARY

The polarography of arsenic(III) in 0.1 or 1.0 M potassium iodide solutions has been studied.

RÉSUMÉ

Les auteurs ont effectué une étude du comportement polarographique de l'arsenic(III), en utilisant l'iodure de potassium comme électrolyte de base.

ZUSAMMENFASSUNG

Schreibung einer Untersuchung über das polarographische Verhalten von Arsen(III) bei Verwendung von Kaliumjodid als Grundelektrolyt.

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CONTRIBUTIONS TO THE COMPLEXOMETRIC DETERMINATION OF CATION MIXTURES

III. SIMULTANEOUS TITRATION OF IRON(III) AND ALUMINIUM IN THE PRESENCE OF AMMONIUM THIOCYANATE AS INDICATOR*

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(Received July 7th, 1960)

The possibility of determining metals by titration of the excess of EDTA with a cobalt solution in the presence of thiocyanate indicator was described by TAKAMOTO²; SEN³ has indicated that it is necessary for $\log K_{MY}$ to be greater than or equal to 15.

Owing to the fact⁴ that $\log K_{CoY} = 16.31$ and $\log K_{AlY} = 16.13$, the reaction



may be possible; hence the end-point may not be stable. But in this titration, as well as when the excess of EDTA is back-titrated with iron(III) solution in presence of salicylic acid or sulfosalicylic acid where $K_{FeY} \gg K_{AlY}$, the end-point is sufficiently stable to be observed, because the decomposition as well as the formation of the aluminium-EDTA complex takes place at a reduced rate.

In the present work a method for the determination of aluminium(III) is described in which excess of EDTA is back-titrated with cobalt nitrate solution in acetone-water medium containing thiocyanate as indicator; the simultaneous determination (in the same solution) of aluminium(III) and iron(III) is also described.

EXPERIMENTAL

The aluminium solution (0.05 M) was prepared from $AlCl_3 \cdot 6H_2O$ and standardized by precipitation of the aluminium as hydroxide and calcination to Al_2O_3 ; the iron solution (0.05 M) was prepared from $FeCl_3 \cdot 6H_2O$ and standardized by precipitation of the iron as hydroxide and calcination to Fe_2O_3 and the EDTA solution (0.05 M) was prepared from disodium ethylenediaminetetraacetate.

PROCEDURE

To 10 ml of solution containing 1–30 mg of aluminium(III) and 0.5–6 mg of iron(III) at pH ca. 2, were added 5 drops of ammonium thiocyanate solution (1%) and the mixture was titrated with 0.05 M EDTA solution until the red color of the solution

* Part II: See ref. 1.

changed to yellow. Iron(III) was thus determined. For the determination of the aluminium a measured excess of 0.05 *M* EDTA solution was then added to the solution. The pH was adjusted to 5–7 with a few drops of a concentrated sodium hydroxide solution and ammonium acetate (1 g) and then a saturated solution of ammonium thiocyanate (1 ml) and acetone were added to the solution. The volume of the added acetone was large enough to give at the end-point of the titration a water–acetone ratio of approximately 1:1. The excess of EDTA was then titrated with 0.05 *M* cobalt nitrate solution; during the titration the yellow color of the solution changed gradually to pink-orange until at the equivalence-point it became blue-green (if the solution did not contain iron the color of the solution changed from pink to greyish-blue). The end-point was reversible. In order to obtain a sharp end-point the excess of EDTA should be sufficient to react with at least 3 ml of 0.05 *M* cobalt solution. If the ratio $[\text{Fe}^{+3}]/[\text{Al}^{+3}]$ exceeds 1/4, the end-point is not sufficiently sharp because the color changes from yellow to greenish-yellow. The results are given in Table I.

TABLE I

<i>Aluminium taken mg</i>	<i>Aluminium found (average) mg</i>	<i>Error (average) %</i>	<i>Iron(III) taken mg</i>	<i>Iron(III) found (average) mg</i>	<i>Error (average) %</i>
2.70	2.72	+0.74	—	—	—
6.76	6.74	—0.29	—	—	—
13.52	13.44	—0.58	—	—	—
27.04	26.86	—0.66	—	—	—
2.70	2.70	0.00	0.55	0.55	0.00
2.70	2.70	0.00	1.37	1.37	0.00
2.70	2.69	—0.36	2.74	2.74	0.00
6.76	6.78	+0.29	0.55	0.55	0.00
6.76	6.76	0.00	2.74	2.73	—0.35
6.76	6.75	—0.14	5.49	5.50	+0.18

CONCLUSIONS

The low decomposition rate of the aluminium–EDTA complex makes possible the indirect determination of aluminium(III) by back-titration of excess of EDTA with cobalt(II) solution in the presence of thiocyanate as indicator in acetonic solution.

When ammonium thiocyanate is used as indicator it is possible to titrate the iron(III) and the aluminium in the same solution if the ratio $[\text{Fe}^{+3}]/[\text{Al}^{+3}]$ is less than or equal to 1/4.

The proposed procedure is simpler than previous complexometric methods^{5,6} for the simultaneous determination of iron(III) and aluminium. It has the advantages of requiring a very common indicator and of being comparatively insensitive to variations in the pH value of the solutions.

SUMMARY

With thiocyanate as indicator iron(III) and aluminium(III) can be titrated simultaneously if $[\text{Fe}^{+3}]/[\text{Al}^{+3}] \leq 1/4$; iron(III) is titrated directly with EDTA, and aluminium(III) is determined by back-titration of the excess of EDTA with cobalt nitrate solution in an acetone–water medium.

RÉSUMÉ

En utilisant thiocyanate comme indicateur, il est possible de doser Fe^{+3} et Al^{+3} sur une même solution, si le rapport $[\text{Fe}^{+3}]/[\text{Al}^{+3}] \leq 1/4$. Dans ce cas, on dose Fe^{+3} par titrage direct avec EDTA et Al^{+3} par titrage de l'excès de EDTA avec une solution de nitrate de cobalt en acetone-eau.

ZUSAMMENFASSUNG

Mit Thiocyanat als Indikator ist es möglich in der gleichen Lösung Fe^{+3} und Al^{+3} zu bestimmen, wenn das Verhältnis $[\text{Fe}^{+3}]/[\text{Al}^{+3}] \leq 1/4$ ist. Man bestimmt das Eisen(III) direkt mit EDTA, das Aluminium indirekt durch Titration des überschüssigen EDTA mit einer $\text{Co}(\text{NO}_3)_2$ Lösung in Aceton-Wasser System.

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Anal. Chim. Acta, 24 (1961) 200-202

Short Communications

Concentrating traces of copper from 1 M ammonium chloride

RICHERS¹ separated traces of transition metals from solutions of 0.1 M ammonium chloride by ion exchange. He passed 2 ml of a solution about $4 \cdot 10^{-4}$ M with respect to transition metal and 0.1 M with respect to ammonium chloride through a 1-ml bed of Amberlite IR-100, a sulfonated phenolic resin. He then removed the transition metals from the resin by washing with 1 M hydrochloric acid. Thus he obtained the following recoveries: 87% copper, 96% cadmium, 95% nickel, 93% zinc, and 87% manganese. This procedure was not successful when the transition metal was dissolved in 1 M ammonium chloride.

The abnormally great affinity of Dowex Chelating Resin A-1 toward transition metals led the authors to try a modification of RICHERS' experiments with this resin. The resin has groups of $-\text{CH}_2\text{N}(\text{CH}_2\text{COOH})_2$ attached to a matrix of crosslinked polystyrene². It consisted of spherical particles, mostly in the range of 40-50 mesh.

A solution was prepared to be $1.58 \cdot 10^{-4}$ M with respect to cupric chloride and 1 M with respect to ammonium chloride. After standardization, this was diluted 1:10 with 1 M ammonium chloride to give a solution 1 M in ammonium chloride and $1.58 \cdot 10^{-5}$ M in copper, or containing 1.00 p.p.m. of copper.

1-1 portions of this solution were passed through columns of the ammonium form of Dowex A-1. The copper was then removed from the columns with 10 ml of 1 M hydrochloric acid and determined by titration with 0.01 M ethylenediaminetetraacetate³.

The results are summarized in Table I. Recoveries of 99% or better were obtained in all experiments except those with bed volumes less than 1.0 ml (numbers 1, 5 and 9) or with flow rates greater than 3.8 cm/min (numbers 7, 8 and 9). It is obvious that

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the chelating resin is much more effective than ordinary cation-exchange resins in the recovery of traces of copper from fairly concentrated solutions of ammonium chloride. The chelating resin will probably serve equally well in concentrating traces of other transition metals from solutions of alkali metals and possibly also from the alkaline-earth metals.

TABLE I
RECOVERY OF $1.58 \cdot 10^{-5}$ M COPPER FROM 1 M AMMONIUM CHLORIDE

No.	Column dimensions cm		Flow rate cm/min	Recovery %
1	1.0	0.94	0.80	96.7
2	1.7	0.94	1.52	99.6
3	1.4	0.94	2.24	99.0
4	1.1	0.94	3.01	99.2
5	1.0	0.94	3.28	98.9
6	1.2	0.94	3.75	99.1
7	1.3	0.94	4.00	93.5
8	1.1	0.94	5.52	93.0
9	1.0	0.94	6.00	88.5

The authors express their gratitude to The Dow Chemical Company, Midland, Michigan, for financial support of this investigation.

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A rapid and sensitive sub-micro phosphorus determination

A method for increasing the sensitivity of the phosphorus determination proposed by FISKE AND SUBBAROW¹ has recently been introduced by BARTLETT². Such increased sensitivity is necessary for the examination of small phospholipid fractions from chromatographic columns, and samples of 50 to 150 μ g organic material can be successfully analysed by this technique. The modification lies² in carrying out the reduction of phosphomolybdate with 1-amino-2-naphthol-4-sulphonic acid (ANSA) at 100° instead of at room temperature and in measuring the absorption at 830 m μ instead of at 660 m μ .

In our experience the method gives good results: the reproducibility is excellent

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and the colour is stable for at least 24 h. A further advantage is that the coloured solution can be diluted with distilled water for measurement in the most sensitive range of the spectrophotometer without loss of proportionality. The sensitivity is 0.1 μg of P (extinction of 0.051 with a 3-cm cuvette). A grave disadvantage of the procedure is, however, that the initial digestion of the sample to give phosphate ion (heating with sulphuric acid at 160–180°) requires 4½ h for completion. Increasing the temperature of the digestion mixture is not favourable because of the risk of loss of phosphoric acid (b.p. 213°). Perhydrol added to decrease the reaction time is difficult to remove completely.

We have found that perchloric acid, as used by ALLEN³ in his method employing amidol as reducing agent, is a better agent for the first step, in that the time necessary for complete digestion can then be reduced to 40 min. (We have established, incidentally, that amidol is not a suitable reducing agent for the development of the colour at 100°, since it gives irreproducible results at this temperature.)

Samples were heated, after the removal of organic solvents, with 0.2 ml of 70% perchloric acid in tubes (125 × 15 mm) standing to a depth of 30 mm in a thermostatically controlled heating block maintained at 180°. The boiling mixture generally cleared after 12 to 18 min heating, and the reaction was completed by heating for a further 20 min. That the reaction was not complete when the mixture first cleared was established by stopping the reaction at this point by rapid cooling; recoveries of only 94–97% were obtained.

Using the described 40-min digestion procedure, and the method of colour development as recommended by BARTLETT, we obtained the following results for a solution of tritotyl-phosphate of high purity (May and Baker Ltd.) in methanol (see Table I).

TABLE I

P added (μg)	P found (μg)	Recovery (%)
1.09	1.11	101.8
1.81	1.81	100.0
2.54	2.51	98.8
3.63	3.64	100.3

It is suggested that the modification of the digestion procedure described should enhance considerably the usefulness of the sensitive BARTLETT determination.

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¹ H. C. FISKE AND Y. SUBBAROW, *J. Biol. Chem.*, 66 (1925) 375.

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Chromatographie von Sterinen, Steroiden und verwandten Verbindungen

Von

R. NEHER

Forschungslaboratorien der CIBA A.G., Basel (Schweiz)

Der Zweck dieser Abhandlung über ein Gebiet von allgemeinem chemischen, biologischen und pharmazeutischen Interesse ist auf die praktische Arbeit gerichtet. Alle für Steroide bewährten Methoden sind so behandelt worden, dass es möglich ist ohne Originalliteratur auszukommen. Säulen- und Papierchromatographie, Adsorptions- und Verteilungsprozesse wurden getrennt behandelt, wobei jeweils die relative Nützlichkeit der einen oder anderen Methode angegeben wurde.

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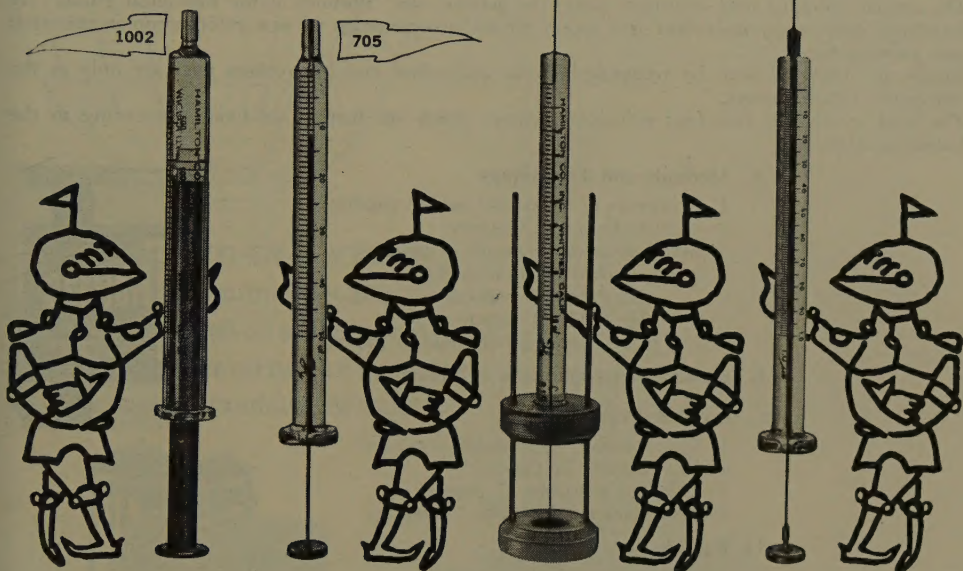
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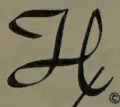


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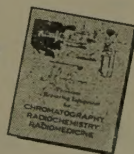
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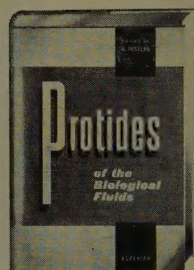
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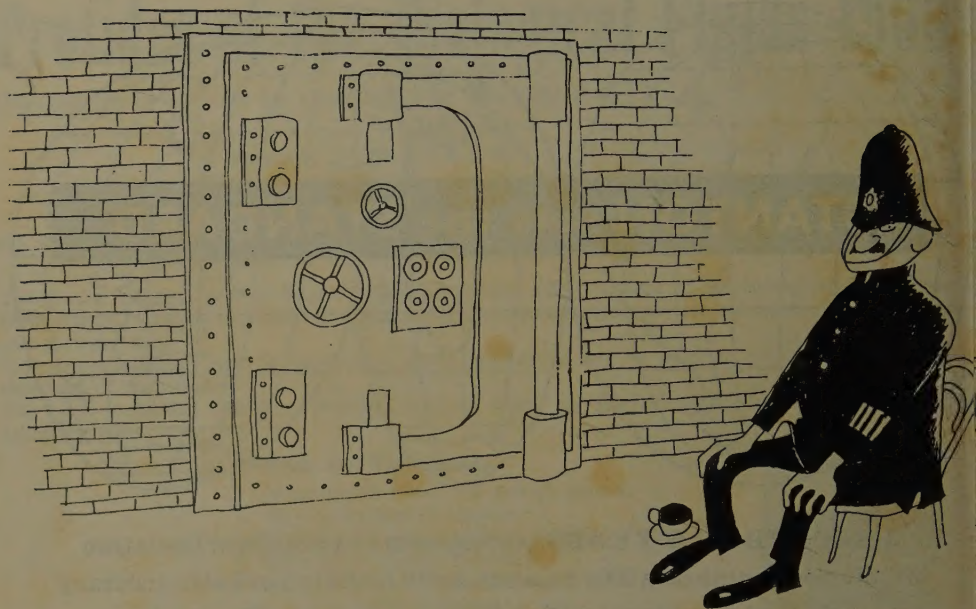


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